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THE ROLE OF DIFFERENTIAL THERMAL ANALYSIS IN MINERALOGY AND GEOLOGICAL PROSPECTING

By

M. FÖLDVÁRI-VOGL*

HUNGARIAN STATE GEOLOGICAL INSTITUTE, BUDAPEST

In this work the author has the intention to giving an introduction for the application of d. t. a. in mineralogy and geology and, on the other hand, she sums up the results of Hungarian investigators.

In Part I the author deals with the theoretical bases of the method, then she follows up by the description of d. t. a. sets. She also describes the apparatuses constructed by herself and her collaborators.

The second part of the work, which is the most ample one, treats d. t. a. of several minerals. Minerals are treated in systematical order. In connection with various types of thermograms, the author calls attention to possible anomalies. Her own experiences are demonstrated by examples given of Hungarian occurrences.

The last part of the paper deals with other practical applications of d. t. a.

The author has inserted a great number of thermograms in order to facilitate the identification of minerals for geologists.

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Preface

In the course of the last decades, differential thermal analysis became more and more general, and at present it may be considered as one of the usual methods for material testing. The general use of this method is due to the fact that, on one hand it furnishes information on the material in a relatively short time — moreover, this information being very valuable and hardly attainable by any other method — and, on the other hand simple investigations can be carried out by simpler instruments, by inexpensive, possibly even home-made apparatuses, consequently d. t. a. examinations do not encounter financial difficulties.

The advantages of d. t. a. at first appeared in connection with the investigation of clay minerals which are hardly determinable otherwise. At present d. t. a. has become widely applied in many disciplines, e. g. to follow chemical processes, but it is used as microcalorimeter for the determination of reaction heats or combustion heats too. D. t. a. as a method for material testing, has also taken a very important part in mineralogy and geology. In complex geological

or mineralogical-petrological investigation of materials d. t. a. is usually employed among the used methods of examination, but some mineralogical-petrological problems may often be decided by applying differential thermal analysis in itself, and some minerals are determinable with absolute certainty in many cases.

As on the basis of certain new theoretical considerations we have introduced an apparatus furnishing more exact data than those so far used, a critical systematization and revision of the data given in various special papers seemed to be desirable by means of this apparatus.

Since d. t. a. of late years has begun to be more and more current in Hungary in the fields of mineralogy, petrology, and even, recently in petroleum geology and coal petrography, we thought of rendering a service by summarizing all that can facilitate the work of specialists, carrying out differential thermal analysis, and of those utilizing and evaluating the results of d. t. a. In order to facilitate the work of our colleagues, we have treated a number of thermograms compiled on one hand from the curves which we found in special literature referring hereto, and on the other hand obtained from the materials of this country. The examinations of Hungarian materials published in the present paper have been carried out partly at the Hungarian State Geological Institute, partly at the Petrographical and Geochemical Department of the Roland Eötvös University.

Miss V. KOBLENCZ assisted us in the systematization of the thermograms.

The specification of the d. t. a. apparatuses has been worked out by Mr. B. KLIBURSZKY.

We hope that by this paper we will further advance the spreading of our method and, perhaps, we may suggest new ideas concerning its application in new fields.

We owe many thanks to Professor E. SZÁDECZKY-KARDOSS, member of the Hungarian Academy of Sciences, who suggested the writing of this paper, supported us in our work, and made its publication possible.

History of differential thermal analysis

Differential thermal analysis was first applied at the end of the last century in the domain of metallurgy, but at about the same time, in 1887, LE CHATELIER had begun to apply this method for the determination of minerals, especially clay minerals. The initiative of LE CHATELIER, however, could not become wide-spread for decades, for until 1942 but a few researchers applied it in our discipline. E. g. about the nineteen-twenties KURNAKOV and his school applied thermal analysis to solve a number of mineralogical-petrographical problems, and they computed lattice energies from the data of thermal

analyses too. ORCEL and his collaborators had also obtained important results in applying d. t. a. to mineralogy, in the thirties of this century. A wide application of d. t. a. may be reckoned with since the publication of several works by NORTON, in about 1940. The growing interest in this method, is to be attributed to the fact, that the internal structure of clay minerals became more and more accurately known at the same period, consequently all methods in connection with clay mineral examination began to develop. Similarly, the investigations of GRIM and HENDRICKS had been published about 1940, then in 1945, SPEIL treated the theory of the physical processes of our method, while KERR and KULP developed this theory by some modifications.

Because of the rapid spreading of this method, we should enumerate many more researchers who have obtained some important results by the application of d. t. a., but this enumeration would lead to unnecessary lengthiness here. Informations will be given in connection with several detailed investigations, or in the bibliography compiled at the end of this paper, for those who are interested in further data.

In Hungary, d. t. a. had first been applied in 1950, for the investigation of clay minerals and bauxites, at the Chemical Department of the Hungarian State Geological Institute. Shortly afterwards investigations by d. t. a. have been introduced at the Heavy Chemical Industry Research Institute of Veszprém and in the Mineralogical-Petrographical Department of the Roland Eötvös University. At present, d. t. a. equipments are already in operation in some 15 scientific, industrial, and university research institutes.

In particular, we have to mention the activity of the Department of General and Analytical Chemistry of the Polytechnical University of Budapest. D. t. a. was applied here first for the structural investigation of analytical precipitates, then it was completed by thermogravimetric measurements, finally a new branch of investigation has been established by introducing differential thermogravimetry [32, 33, 34].

I. GENERAL PART

Fundamental principles of differential thermal analysis

In principle, d. t. a. is based upon observing or rather measuring the heat which is produced or absorbed, respectively, when, during heating or cooling, the substance examined is subjected to physical or chemical alterations consequent upon changes in the heat content. In all types of d. t. a. equipments which are at present in use, the observation of the heat produced or absorbed is practically in accordance with the solution initiated by ROBERT AUSTEN and developed by HOULDSWORTH and COBB. Essentially, it consists in heating

or cooling an inert substance under the same thermal conditions and simultaneously with the substance examined. Aluminium oxide is mostly used as an inert substance, but in many cases after previous annealing the sample itself may be employed. The advantage of the latter is, that the thermal conductivity of the substances placed in both holes is more similar than in case of a substance of a totally different kind in the other hole, but the annealed substance itself cannot be used as an inert, if a reversible thermal process also takes place in the sample.

The difference in temperature between the sample and the inert substance is measured by means of differential thermocouples. The differential thermocouple indicates temperature differences when heat-producing or heat-absorbing processes are taking place in the sample. The rate of temperature difference

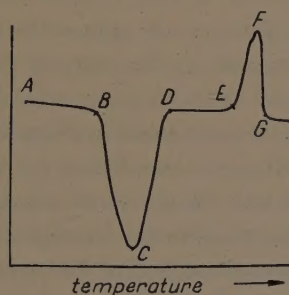


Fig. 1

is a function of the heat produced or absorbed. We obtain the d. t. a. curve by recording the current generated by the differential thermocouple or, when such recording is not possible, by noting the deflections of the galvanometer switched on the circuit of the differential thermocouple, and plotting them as a function of actual temperature. Consequently, the shape of the thermogram is horizontal where there is no alteration in the substance, and deflections, the so-called thermal peaks are to be seen in the curve where alterations consequent to changes in heat content are taking place. Conventionally, d. t. a. curves are drawn in such a way, that the peaks marking heat absorbing, endothermal processes should appear below, while the peaks representing exothermal processes above the base line.

As the thermogram of a mineral, chemical compound, inorganic or organic substance is characteristic to the substance in question, it enables us in recognizing the presence of that substance. The details of the determination will be exposed in connection with the description of d. t. a. curves of several minerals.

In fig. 1 a typical thermogram is presented, with one endothermal and one exothermal peak. On section AB no alteration takes place in the substance, B signifies the starting point of the endothermal process, D the end of the endo-

thermal process. On section DE there again is no process accompanied with change in the heat content, until the beginning of the exothermal process.

As the magnitude of the peaks of the thermograms is a function of the heat produced or absorbed in the course of the process, further conclusions may be drawn from the curve, in addition to the identification of the substance, generally based on the temperature of the peaks. On one hand, we can conclude the magnitude of heat of dissociation, heat of dehydration, heat of alteration of a substance, and, on the other hand, to the quantity of a substance present in unknown concentration.

Theory of the thermal processes of differential thermal analysis

The effort of applying d. t. a. for quantitative determinations too and, in addition, the increasing demand on accuracy of these determinations necessitated a more thorough study of the heat process taking place during the investigations. The first theory was established by SPEIL in 1945 [158]; some years later it was developed and partly modified by KERR and KULP [81]. The aim of the SPEIL—KERR—KULP-theory is to establish a relation, expressible by reduced equations in order to give the changes in heat content of the substance exposed to thermal alteration and of the inert substance, at every point of the thermogram. During the development of a thermal peak, the value of the complete reaction heat may be expressed by the following integral

$$M(\Delta H) = g \cdot k \int_a^c \Delta T dt$$

where M signifies the mass of the reaction substance, k its specific heat conductivity, g a geometrical constant, ΔH the specific change in heat content, and $\Delta T dt$ the change of temperature in function of time (t), during the process, measured in the middle of the sample. The limits of integration mark the starting point and the end of the peak.

Naturally, this relation is but approximative, and many accessory factors, as e. g. the temperature gradient taking place in the sample, are not taken into consideration. It is, however, very useful as a first approximation, and for that very reason, the most widely accepted relation.

In the theoretical considerations of MARJORIE J. VOLD [168], the thermal process taking place in the substance is calculated with a regard for many more accessory factors; this consideration comes closer to reality, but because of the less simpler form of its mathematical formulae it is not generally accepted. VOLD has computed the velocity of heat capacity in the sample and the inert substance, besides taking into consideration the loss caused by the heat radiated in the environment. In case of thermally active samples, the author has taken

into account, as a separate additive member, the heat produced or absorbed by the alteration taking place in the sample. Her final result has been a differential equation which, by taking into consideration all accessory factors, gives us the possibility of numerically calculating the change of heat content taking place in the sample.

A series of papers have been published last year on the kinetics of thermal dehydration of clays by MURRAY and WHITE [119]. A chapter of these publications describes the kinetics of the d. t. a. process.

The kinetical formulation of the processes has led the authors to the conclusion that d. t. a. and d. t. g. (differential thermal gravimetry) curves may theoretically be approximated by graphical integration of the relations referring to isothermal partial processes. The curves calculated in this way and the real curves were concordant. Further, the effect of changes of the parameters on the shape of d. t. a. and d. t. g. curves has also been interpreted.

All these theories give mathematical formulations of the thermal processes, but they do not present any adequate basis for the construction of d. t. a. apparatuses. Such a basis is, however, necessary because contradictions among thermograms produced by different d. t. a. apparatuses are very often to be observed; that can be attributed not only to certain differences of the samples (e. g. differences in degree of crystallization and purity, genetical differences etc.) but to discrepancies of principle among the apparatuses.

It is obvious that concordant results are not to be expected, except from such apparatuses constructed on the basis of uniform principles. The author of the present paper and her collaborators have tried to determine the guiding principles of construction of a d. t. a. apparatus. First of all, they tried to follow the processes which took place in the sample and in the inert substance during heating. In order to give a clear idea of their considerations, they chose the graphical method of representation [44].

The train of thought used is briefly the following. Let us imagine two holes of identical dimensions, symmetrically placed in the nickel sample holder block; the sample is placed in one of them, the inert substance in the other, the density of both being as uniform as possible. After having placed the sample holder block in the furnace, and heating the furnace at uniform speed, let us consider what heat processes are taking place in the holes.

If the rise of temperature in the sample holder block itself is represented in a coordinate system, as a function of time, we obtain a steep straight line, marked by *X* in fig. 2.

The rise in temperature of the inert substance placed in the hole is represented by a straight line parallel to the straight *X*, in its stead let us consider the straight *X* itself. Naturally, heating does not take place in reality along straight lines but along sections of exponential curves following each other, and it is only in first approximation that they can be drawn as straight.

into consideration the solutions so far applied, when the temperature is measured in the inert substance, the temperature of the peak of the thermogram (point *B*, in fig. 2) will not be measured as T_1 — which is the real temperature — but as $T_{\max 1}$, to be seen in the figure. E. g. BARSHAD [6] has acknowledged the importance of controlling the temperature of the process in the decomposing substance itself, therefore he put in the hole, below and above the sample investigated, two substances of different and known temperature of alteration, thus restricting the real temperature of alteration of the sample investigated between two definite limits. According to literature, only the thermograms

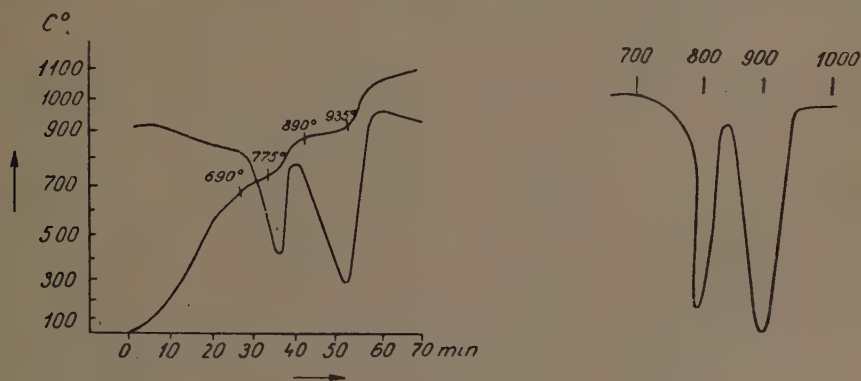


Fig. 4

of Soviet authors refer to having measured the temperature in the sample itself but, as far as we know, they have not motivated their working method. It is instructive to compare two d. t. a. records taken from the same mineral, but according to the two ways in measurement (fig. 4).

Both thermograms of this figure have been recorded from dolomite, the left-hand curve has been published in the paper by L. G. BERG, the right-hand one in the paper by R. A. ROWLAND and C. W. BECK [12, 141]. The first endothermal peak of these d. t. a. curves is derived from the decomposition of magnesium carbonate, the second from that of calcium carbonate. Naturally, the magnitudes of the peaks of the curves are not to be compared, because the investigations have been carried out by means of two apparatuses of unknown sensitivity. In the figure of BERG, the second curve running steeply above the d. t. a. curve, derives from a current recording of the rise in temperature, photographed simultaneously with the d. t. a. curve. It appears that the rise in temperature has really been measured in the sample itself, for smaller failures are to be seen in the continuous rise of temperature at the very places of the great endothermal peaks. An enlargement of the latter curve would at fact represent the same as the curve *OAB'CX* of fig. 3 in our theoretical consideration. The dolomite curve of BECK has been drawn by the usual method.

The maximal temperature of the peaks, if it is measured in the sample itself, gives a little lower value than the temperature measured in the inert substance. The direct explanation of this fact may be read in fig. 3, for it is obvious that $T'_1 < T'_{\max}$. According to our experience, the deviation is about 20°C , and we have to mention in advance, that in our thermograms of Hungarian materials, the maximal peak temperatures are, at about the same rate, lower than those published in the literature, but in our opinion this lower value comes closer to the real temperature of alteration. All these argumentations refer to endothermal peaks, while exothermal peaks are a little shifted to higher temperatures, on the basis of similar considerations.

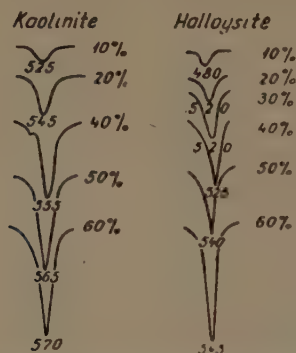


Fig. 5. Endothermal peaks of kaolinite and halloysite diluted by aluminium oxide

There are some further advantages of measuring the temperature in the sample itself. Everybody dealing with d. t. a. may observe that, in the thermogram, the maximum temperatures of the peaks appear as a function of the amount of active substance present. The lower the concentration of the active substance present, the lower will the peak maximum be. L. A. DEAN [27] studied e. g. the change of the endothermal peak of kaolinite and halloysite, between 550 — 600°C , in function of the concentration. As it is to be seen in fig. 5, the d. t. a. curves of the samples containing 10% and 60% of kaolinite, show 45°C departure between the maxima of endothermal peaks.

The interpretation of this phenomenon may be illustrated by figs. 2 and 3. In fig. 3, the length of the straight AB' depends on the amount of active substance. Let the point B_2' signify the peak maximum of a thermal process belonging to a larger amount of substance. If we measure the temperature in the inert substance, it is obvious, that in the first case T_{\max_1} will be observed as the temperature of peak maximum, T_{\max_2} being observed in the second case. Conversely, if temperature is measured in the sample itself (fig. 2), we should ideally obtain T_1 as peak temperature in both cases, irrespective of the amount of substance, in reality (fig. 3) there is but little departure between the two peak temperatures, this difference being represented by the distance ΔT_2 .

Our theoretical considerations have been justified by experimental data. Since we have been measuring temperature in the sample itself, we observed that instead of peak-temperature differences of 40—50°C deriving from discrepancies in concentration, the peaks were only shifted from 10 to 15°C.

It is quite natural that the author and her collaborators are aware of a great number of defects of the considerations above described, for they but follow the outlines of the heat processes taking place in the hole, and do not take into account, e. g., of the propagation of heat in the sample or in the inert substance. However, if we took the accessory factors into consideration, the graphical representation of the process would not be clear anymore.

The theoretical considerations treated hitherto referred to the interpretation of heat processes taking place in the substance. It is, however, absolutely necessary to know all further factors which play any part in the formation of the d. t. a. curve. One of the important factors which must be dealt with, is the particle size of the substance to be investigated.

All investigators dealing with differential thermal analysis can observe that the particle size of the sample has an effect on the shape of the thermal peaks, and, in some cases, it may even modify the temperature of peak maximum. E. g. J. L. KULP and A. F. TRITES observed the temperature of the endothermal peak maximum marking the alteration of goethite, while changing the particle sizes. Their results were summed up in following table [98] :

Particle size	Peak temperature
Coarser than 50 meshes	405 °C
50 to 80 meshes	405 °C
80 to 100 meshes	400 °C
100 to 120 meshes	400 °C
120 to 200 meshes	395 °C
Finest powder	390 °C

In some extreme cases, the increase of powdering can substantially change the thermogram, in such cases, however, the change is caused by the breakdown of the crystal lattice. We shall return to this phenomenon, in connection with the thermal analysis of dolomites.

In clearing up the mechanism of thermal processes this makes it also possible to theoretically explain the effect of particle sizes on the formation of the peaks. It is obvious that during the alteration of a substance, smaller particles are altered sooner than the larger ones, for time is required for the propagation of alteration into the interior of the particle, especially when, similarly, time is required for the departure of the decomposition products

(vapour, carbon dioxide, etc.). Consequently, if very fine particles are present, the beginning of decomposition (point *A*, in fig. 3) takes place a little sooner. If the particle size of the sample were ideally homogeneous, all particles would, in principle, decompose simultaneously, naturally, leaving aside the fact that time is also required for the propagation of heat in the substance, from the walls of the hole into the middle of the hole. I. e., generalizing this statement, in case of homogeneous particle size, the decomposition would take place along the straight *AB* of fig. 2. This would appear in the d. t. a. curve itself in the form of narrow, pointed peaks. On the contrary, the more heterogeneous the particle size of the sample, the more are the peaks stretched. Graphically, the more heterogeneous the particle size of the sample, the more steep will the straight *AB'* be in fig. 3.

Summing up our considerations, we may point out that the initial temperature of decomposition is determined by the decomposition temperature of the finest particle present in the sample, and, on the other hand, the distribution of particle sizes has an effect on the form of the peaks in such a way, that the more heterogeneous the particle size of the sample, the broader (and at the same time, plainer) should the thermal peak be stretched. Naturally, the deformation of the peak has, in principle, no effect on the extent of the peak area.

A further factor affecting the shape of the thermogram, is the material of the sample holder block. E. g. in the case of a sample holder block made of a material of lower heat capacity, the block absorbs less of the heat produced during exothermal processes, consequently in such a case the exothermal peak will be higher. Inside the block, however, the formation of thermal stability can be more assured by a block made of a material of higher heat capacity. On this basis, after due examination of these different advantages, there exists a difference of opinion among the investigators, concerning this problem. E. g. according to GRUVER and his collaborators, sample holders of low heat capacity and high heat conductivity are more advantageous, they therefore used a platinum crucible as sample holder. On the contrary, some other researchers accentuate the advantages of the sample holders of high heat capacity and low heat conductivity, and employ ceramic sample holders.

The magnitude of the thermal peak is considerably affected, under identical sensitivity of the instruments, by the heat capacity of the applied thermocouple too. It is obvious, that the decrease of heat capacity of the thermocouple increases the magnitude of the peak and, at the same time, the sensitivity of determination. All these factors will be dealt with in detail, in connection with the description of the different types of apparatuses.

In case of thermal processes producing some kind of gaseous products, it is thermodynamically probable that the process and, at the same time, the shape of the thermal peak will be considerably affected by the rate of the partial

pressure of the gaseous products exerted on the decomposing substance. The effect of gas pressure on thermal decomposition has been studied by R. A. ROWLAND and D. R. LEWIS [143]. A part of their experiments concerns the decomposition of carbonates. They have observed the changes appearing in the temperature — and often in the shape — of thermal peaks, taking place either in the air or in an atmosphere of CO_2 . Their results are graphically represented in fig. 6. The effect of CO_2 on the changes of peak temperature is directly readable. In the air, the decomposition of siderite is immediately followed by the exothermal peak marking the oxidation of bivalent iron, which naturally, does not occur in the atmosphere of CO_2 . The particular behaviour

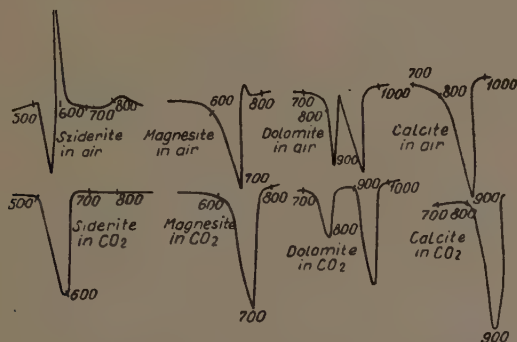


Fig. 6

of dolomite to be seen in fig. 6 (the temperature of the first peak decreases in the atmosphere of CO_2) will be treated apart, in the chapter dealing with the thermograms of several substances; this phenomenon is a part of the observations concerning the peculiar decomposition of dolomite.

It has already been observed, in connection with the curves of ROWLAND and LEWIS, that the shape of some peaks may considerably change and even disappear, if the investigation is not performed in air, but in an inert atmosphere. This statement concerns every kind of combustion and, in general, oxidation processes. Naturally, when the investigations are being carried out in vacuum, the peaks change considerably. In this case, every process involving loss of steam or gas is considerably accelerated, in consequence of immediate going out of the product originated: this appears in the thermograms in the form of narrow, pointed peaks.

The effect of the density of the sample on the shape of thermal peaks is due to similar causes of principle. Namely, if the powder of the sample is loosely placed in the hole, the gaseous products originated during decomposition will more easily escape; on the contrary, if the sample is very condensed in the hole, the remaining gaseous products will retard, by their pressure, further

decomposition. Consequently, in the case of loose density we obtain narrower forms of peak than those obtained from substances condensed in the hole. From this phenomenon, we may draw the conclusion, for the purpose of practice, that in order to assure reproductibility, the powder of the sample should be condensed in the hole as equally as possible.

The shape and position of the thermal peaks are affected by the velocity of heating too. Our experiments referring hereto will be treated in detail in connection with the data concerning one of our apparatuses.

We do not treat here the effects of the presence of another mineral, which may disturb the formation of the thermal peak. The other mineral may disturb the formation of a peak by altering, under the effect of heat, in the same domain of temperature and thus the peaks overlap partially or entirely, but it is also possible that the presence of some substance should affect the formation of the thermal peak for reasons known or unknown hitherto, without taking part in the alteration. We shall return from time to time to this phenomenon, when d. t. a. curves of several minerals will be treated.

After having drawn the conclusions concerning the thermal process and in full knowledge of the factors affecting the formation of peaks, it becomes obvious that the initial temperature of thermal peaks (point *B*, in fig. 1) will be more characteristic to the substance thermally altered than the temperature of the peak maximum. Since the latter datum is, however, more frequent in the literature, we more frequently mark peak temperatures in the description of thermal peaks of several minerals, but initial temperature can be read in the figure.

From the foregoing argumentation it appears, that many accessory factors must be taken into consideration in the course of d. t. a. investigations and when evaluating the thermogram, if we want to obtain reliable results. This must be in an increased degree applied, if we have the intention of carrying out quantitative determinations on the basis of d. t. a. curves.

Basic principles of quantitative d. t. a. determinations

From the relations established by SPEIL-KERR and KULP (see p. 8) it results that, during a thermal process, the change in quantity of heat is proportional to the area included by the peak. Since in case of the same substance the change in temperature measured in the course of the thermal process is in direct proportion to the amount of the substance present, it follows that the peak area must be considered as the measure of the quantity of the mineral present. However, it must be again emphasized that not every thermal process will be serviceable for quantitative determinations, but only those processes which are unequivocally characteristic to the structure of the mineral in question.

Some investigators consider the length of the altitude of peak amplitude as being proportional to the quantity. In an ideal case, it would really give a correct result, but the perfect constancy of all experimental conditions would be required for that purpose, which is unattainable in every case, even with the utmost care. Thus a small departure in the velocity of heating or in particle size may cause some changes in the peak altitude, but the extent of the peak area is less affected by these factors.

It is obvious that thermal peaks obtained by means of different sets can not be compared for the purpose of quantitative determination, because the magnitude of the peak considerably depends on the data of the apparatus and on the sensitivity of the instruments. Consequently, the apparatus must be calibrated for every quantitative determination, i. e. the sizes of peak areas belonging to known amounts of substance must be determined. Moreover, in many cases, the calibration has to bear out the rate of heat corresponding to a peak area, measured by the equipment in question.

Before treating calibration, we have to particularly emphasize the scrupulous care which is necessary for quantitative determinations. All factors affecting the shape of the peak must be taken into consideration. We have to take care of the constancy of heating velocity. The powdered samples are to be weighed carefully, and when we are filling them in the hole, we must be careful that their density should remain uniform. It is required that the pulverization should always be carried out in the same fineness. We must pay attention to the thermal symmetry of the equipment. The junctions of the thermocouples are to be placed in the very middle of the holes, the sample holder block in the thermal symmetry axis of the furnace. In case of measurements of the same kind, identical conditions are required for the escape of vapours or gases produced during the process.

The possibilities of quantitative d. t. a. investigations have recently been discussed in detail by VAN DER MAREL [118].

The generally used calibration of the equipment for quantitative determination is carried out in such a way, that we prepare a series of artificial mixtures of varying percentage of the mineral to be determined and of some thermally inert substance, then after having determined the peak areas corresponding to different percentages of composition, the unknown percentage of the mineral in question becomes determinable by interpolation, by means of the obtained values. For the purpose of the preparation of the series of mixtures, we use a very pure or purified natural occurrence of the mineral, or we prepare it artificially.

There are considerable differences of opinion among the investigators concerning the accuracy of quantitative determinations. That is quite natural, for it depends on the substance itself and, on the other hand, on the sensitivity and reliability of the equipment, furthermore on the possible effect of other

minerals which are usually present. In the best of cases, the relative error of determination does not exceed 1 to 2% but, generally, it is 5% or even more. In case of the determination of a mineral of a very small amount, the inaccuracy of quantitative determination will be very high, even if the high sensitivity of the instruments permits the identification of the mineral.

Another method of calibration of the instruments consists of determining the relation of the heat produced or absorbed during the thermal process to the peak area. Such measurements were carried out by I. BARSHAD [6]. He departed from substances of known fusion heat. Instead of planimetering the peak areas, he cut out the paper along the outlines of the peak and then weighed the slip of paper of the peak area by an analytical balance. The result was a number giving the relation between the heat and the weight of the slip of paper encircled

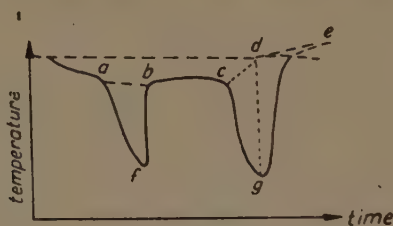


Fig. 7

by the peak. After having found out that, supposing the paper to be of uniform thickness, this weighing method gave accurate results, he tried out the practicability of the method on some processes producing known changes in heat, and he has obtained data in accordance. Further he proposed that — taking also into consideration the differences of heat processes — the calibration should be based on the dehydration of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the case of water absorbing processes, and on the heat absorbed during the decomposition of AgNO_3 and CaCO_3 in the case of decomposition processes. This method may be good to draw a comparison between data of two different apparatuses.

Yet, quantitative d. t. a. investigations even performed with the utmost care, encounter some further difficulties. One source of error has its origin in the measuring of the peak area, for, many times, the base line of the peak area is not well definable, as in many cases the base line marking repose after a peak does not return to the original position, but it continues below or above the original base line (see fig. 7).

This phenomenon may be explained by the fact that, after the thermal process, e. g. in the case of dehydration, the substance loses its original crystal modification and, thereupon, changes are taking place in its heat conductivity. Now the question is raised of the starting base line to be taken into consideration in measuring the peak area. L. G. BERG [13] has dealt with this problem and

he proposed the following graphical solution: he drew a normal from the peak maximum in the horizontal direction (fig. 7), then connected the point of intersection d with c and e , i. e. with the starting point and end of the peak. According to his solution, we proceed rightly by considering as peak area the area limited by the curve cge and straights cd and de .

Another difficulty of quantitative determinations occurs when in a substance consisting of multiple constituents there are two components, the thermal processes of which take place at about the same temperature, i. e. their peaks are partly or entirely overlapping. L. G. BERG solved the measuring of the area of not perfectly distinct peaks by a graphical method, similar to the preceding one, as it is to be seen in fig. 8.

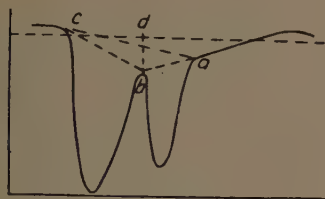


Fig. 8

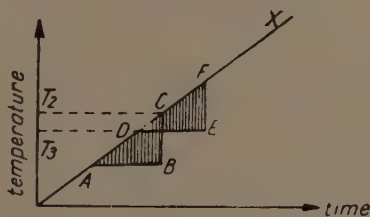


Fig. 9

The author and her collaborators tried to surmount the difficulties of quantitative determination. If we graphically represent the thermal processes, as it is exposed in the theoretical part of this paper in figs. 2 and 3, two subsequent and not perfectly distinct thermal processes may be represented in such a way, as to be seen in fig. 9.

The peaks of the two processes distinctly appear if the final temperature of one process (T_2) is lower than the initial temperature of the following process (T_3). Conversely, if T_2 is higher than T_3 , a partial overlapping takes place, as is to be seen in the figure. Since it follows from the theoretical considerations that both the maximum and the end of the peak depend on the quantity of the substance in question, consequently — by reducing the amount of the substance investigated — we often succeed in reducing the temperature T_2 to such a degree, that it should become lower than T_3 , and thus the two peaks appear distinctly. If the peaks are so close to each other that this procedure is no more serviceable, the author and her collaborators are employing the following method for the solution of the problem [44]: Let us place the substance of multiple components to be investigated, in one of the holes of the sample holder block, while we intermix in the other hole, not only the inert substance, but also the component disturbing the determination. After some experimental attempts, we may succeed in intermixing in the inert substance, about the same amount of disturbing components as that present in the sample; in such a case, in con-

sequence of the opposed heat processes, the peak of the disturbing component disappears from the thermogram. By means of this method, the peak of the other component becomes measurable, and, if necessary, the amount of the disturbing component can also be given in connection with this procedure.

Let us show an example for the application of this method. In case of bauxite investigations, it frequently happens that, between 500 and 600° C, the endothermal peaks of boehmite and kaolinite do not appear distinctly, there are but 20 to 30° C of departure between the two. E. g. if we have in view the determination of the amount of boehmite, the disturbing peak of kaolinite must be eliminated from the thermogram. In this case, kaolinite must be intermixed in the inert substance, possibly as much as the kaolinite content of the sample to be investigated. The amount of kaolinite present is

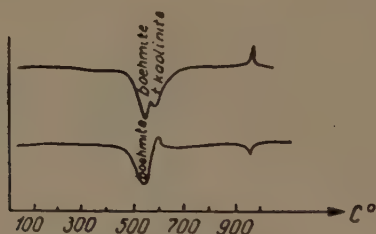


Fig. 10

determinable by a crude approximation in an informative record, if we know the percentage of area corresponding to the kaolinite peak, with reference to our apparatus. The determination is not disturbed by intermixing a little more kaolinite in the inert substance than that present in the sample, for in this case, a small "exothermal" peak appears at the same place, instead of the usual endothermal peak of kaolinite, by which the evaluation will not be disturbed. This procedure can be seen in the thermal curves of fig. 10 where the small exothermal peak in place of the kaolinite peak, marks that a little more kaolinite has been used for compensation than the amount present in the sample.

This compensating method is serviceable even in the case of perfectly overlapping peaks. In such a case it is possible to eliminate by compensation those components, the presence and amount of which have been determined apart, by means of other methods.

This method (briefly compensating method) has also been employed by the author and her collaborators in order to increase the accuracy of the quantitative method. The procedure is the following: The amount of the mineral component investigated is determined by planimetering the peak area, by means of a previous informative record in the usual way, and with the usual accuracy. Afterwards we prepare an artificial mixture containing the predetermined

amount of the component in question. This mixture is placed in place of the inert substance. Now we carry out the record anew, using the high sensitivity of the galvanometer. If a deflection appears in the place of the peak in question, that will be the measure of departure existing between the two percentages of composition and, at the same time, it in fact represents the error of the first determination. By measuring the area of this deflection we may rectify the first crude result. We have succeeded in considerably increasing the accuracy of the determination by that method.

In many cases, the compensating method has proved advantageous so far as identical substances were placed in both holes, their heat conductivity was changing in connection with the thermal process in the same, and, thus, after the peak, the base line came closer to its original position.

A special application of the compensating method becomes possible when a gradual change of the mineral composition should be followed in successions of geological strata. If samples of two successive strata are placed in the two holes, the thermogram gives directly the change of mineral components, in conformity with the succession of strata.

However, quantitative d. t. a. investigations are not always reliable, even if one takes all factors into consideration, for there are some internal factors which are not eliminable. These internal factors originate either from differences existing in the internal structure of the substance or, as it often occurs, the thermal process is affected by some accessory substance which in itself is not subject to any thermal alteration. Such cases will be pointed out later.

D. t. a. apparatuses

No uniform type of apparatus has yet been developed for the purpose of differential thermal analysis. Several investigators or groups construct their respective equipment according to their special aims, in accordance with their principles. Since there is no uniform type of apparatus, it often happens that one finds in the literature departures concerning the magnitude, and even the temperature of the peaks of thermograms of the same substance, if the investigation has been carried out by two different equipments.

The first investigations of LE CHATELIER were not yet performed by the differential method later developed. He heated in a furnace uniformly and rapidly the substance investigated and, meanwhile, measured the rise of temperature in the substance by platinum-platinum rhodium thermocouples. He photographed the light beam reflected from the mirror of a galvanometer connected with the thermocouple at intervals of 2 sec. Supposing that the heating of the furnace is in fact uniform, the light signals photographed at intervals of 2 sec will be equidistant. On the other hand, if the heating of the

substance is retarded by a heat-absorbing process, the intervals become shorter, while they become wider if the substance is rapidly heating in consequence of a heat-producing process.

The connection principle of differential thermocouples was first applied by ROBERT AUSTEN, for the investigation of metals and metal alloys.

In 1913, LE CHATELIER again presented at a session of the French Academy, in Paris, a paper by R. WALLACH, dealing with the thermal investigation of clays. Here we already see the thermograms which have since then become usual: that fact indicates that the principle of realization of the investigation has already been similar to the actual one, but the shape of the curves however shows that the method was still unaccomplished [169].

Up-to-date d. t. a. investigations are based on a solution employed in 1923 by HOULDSWORTH and COBB [75]. In this way, one has to heat a substance which does not alter on thermal effect, under the same conditions and simultaneously with the sample investigated; the change of temperature of the sample investigated is to be measured in relation to this comparative sample, and not to the temperature of the furnace, as was the procedure of former investigators.

This principle determines the most important parts of the apparatus, required for carrying out our method, there are only a few changes in the execution of certain details.

First of all, a furnace is required for a d. t. a. apparatus, for the purpose of heating the sample. Further essential parts of the apparatus are the following: a sample holder in which we place the sample investigated and the standard substance, a thermocouple for measuring the temperature or the difference in temperatures, respectively, with the instruments belonging to them. In most cases, the instrument is completed by a recording equipment which is, however, to be considered as an accessory part.

Let us take the parts of the d. t. a. apparatus one by one and examine what kinds of solution were found serviceable by various authors and analyse the arguments supporting one or the other of the solutions.

Furnace. The furnaces which are of various types, serve for heating the sample investigated according to the conceptions of various authors. From the simplest type of crucible furnace to silite-rod high-power furnaces, all types were employed. As relatively concordant thermograms have been obtained by means of furnaces of different power and construction, it has been proved that the construction of the furnace was not a decisive factor, when some considerations of principle had been fulfilled. One of the most important requirements seems to be that the distribution of temperature should be uniform in the furnace, i. e. the temperature gradients taking place along the axis of the furnace should be identical. Several investigators tried to fulfil this requirement by increasing the heat capacity and, at the same time, the power of the

furnace. There is no doubt that the uniformity of temperature distribution was insured in this way, but it later appeared, that the furnace was heating slower and the time-pattern control of rise in temperature became difficult. As a result, in order to facilitate time-pattern control, direct radiation heating bodies were employed, consisting either of resistance heater (maximum heating capacity about 1100°C) or silite rods (maximum heating capacity about 1500°C).

As for the positioning of the furnace, vertical furnaces having many advantages of construction were the most frequently used by the investigators. In such a furnace, it is much simpler to affix the sample holder, since, because of the vertical arrangement, the parts serving for the fastening are not exposed to lateral load and, at the same time, the concentric or vertical mechanical load of the heater is more favourable. On the other hand, convection currents in a disadvantageous way affecting the thermal symmetries required in the interior of the furnace, take place more freely in a vertical furnace. That is perhaps less frequent in horizontal furnaces but, at high temperatures, lateral loads in an unfavourable way affect the reproducibility of identical arrangements.

If d. t. a. investigations are performed in a vacuum, vertical furnaces are, naturally, rather more in use, for the furnace and the sample holder are placed under some kind of a bell-shaped cap.

The development of the apparatuses trends towards furnaces of a much lower power, because the authors make efforts to insure uniform temperature distribution by other solutions of construction. The 100 W furnace applied by the author and her collaborators at the Hungarian Geological Institute, in their "rapid" d. t. a. apparatus which will later be described, is smaller than any furnace referring hereto published in the literature.

As for the material of hot-wire, the "Kanthal A" has proved to be very suitable; practical experiences concerning its thickness are the following. As the life of hot-wire depends on the watt-loadability of its surface, which in turn decreases rapidly with the temperature of the hot-wire, it seems advisable to apply thick hot-wire. It follows that it is to the advantage of the longevity of the furnace, if the power required is obtained by low voltage and high amperage, i. e. if relatively thick hot-wire is chosen. The current required for heating up is obtained, in this case, by means of a transformer supplying 10 to 20 V, which in turn is controlled by a torroide (variac) transformer, if manual control is employed, but it is advisable to do so with time-pattern controllers too.

Temperature controllers. Every investigator emphasizes that uniform and reproducible heating is a very important factor of d. t. a., especially if quantitative determinations are also carried out. In order to attain uniform heating of the furnaces, various controllers have been applied.

The most simple kind of control is manual timing, by means of a variable resistor or torroide (variac) transformer inserted in the heating circuit. The right adjustment of the variable resistor or transformer can at any time be

controlled by an ampero-meter. The same variable resistance can be changed by means of a clockwork, driven by a uniform speed motor.

This control, however, does not eliminate inequalities originating from line voltage variation which, in the loaded mains of great institutes, may come to 10 or even 20%. As the change of power input is proportional to the square of voltage change, these oscillations may have a disadvantageous effect on the uniformity of heating.

Simple and relatively reliable control is furnished by the controllers equipped with a drop bracket and dials, which function quite well at low power. On the other hand, an unpleasant property of these controllers must be taken into consideration. Namely, it often happens that — in consequence of the wrong positioning of control thermocouples — the control equipment which is only able to switch the power in and out, is disposed to switch in and out at certain intervals, without in fact controlling the temperature.

Electronical time-pattern controllers functioning by back-control or delay, are more accurate and reliable than the above-mentioned solutions. Their operation, however, generally requires special spare parts and skilled, permanent handling personnel. These electronical time-pattern controllers do not only heat the sample, according to a pre-established programme, but they are also suitable for cooling in the same way, which in many cases is a considerable advantage in d. t. a. investigations.

Sample holders. In the course of d. t. a. investigations the sample is placed either in the holes of solid sample holder blocks, or in crucible-shaped holders, or in the metallic tubes encircling the junctions of the thermocouple. According to various authors, the sample holders do not vary only in shape, but in material too.

The choice of shape and material for the sample holder has a considerable effect on the shape of the thermogram, as has been pointed out in our theoretical considerations.

As for the material of sample holder blocks, they are made of metallic or insulating material. It is obvious that in metallic sample holders the distribution of temperature is more uniform, but endothermal peaks are more plain than in case of sample holders made of insulating material. Concerning the problem whether the metallic material of the sample holder should consist of the usual all-nickel or of heat-resistant chrome-nickel steel, our experiences have shown, that chrome-nickel steel of high heat-resistance proved to be more heat-resistant than that of the all-nickel one. In our practice, a sample holder block made of such a material endured more than 1000 heatings, without any change in dimension.

GRUVER [65] employed a platinum sample holder, the heat conductivity of which was even higher than that of the generally used nickel or chrome-nickel steel sample holders.

Ceramic sample holders have indubitable advantages, but one of their greatest disadvantages is that e. g. they are attacked by highly alkaline samples; another disadvantage is that they crack after a certain amount of repeated heating. Naturally, it is easy to replace them, but frequent exchange of the sample holder is disadvantageous, because the adjustment of every new one necessitates repeated calibration of the peak areas.

Some authors do not employ sample holder blocks, but place the sample in crucibles (e. g. VITAL, 167), some others form the sample holders from the junctions of the thermocouple (HEROLD and PLANJE, 73). A more frequent solution consists in encircling the junctions of the thermocouple by a metallic tube and there placing the sample to be investigated and the standard substance.

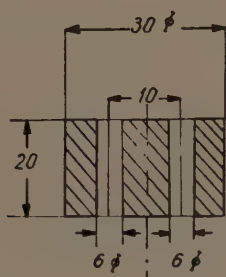


Fig. 11. Sample holder block made of heat-resistant chrome-nickel steel

If a sample holder block is used, two, three, four and in case of parallel determinations, even more holes are employed for the sample and the inert substance. As for the placing of the holes, it must again be taken into consideration, that one has to insure the thermal symmetry between the sample and the inert substance to be compared, i. e. during heating their temperature may not be different, only where alteration takes place in the sample. In accordance to the experiences of the author and her collaborators, thermal symmetry is most easily insured by applying two holes.

Fig. 11 shows the scale drawing of a chrome-nickel steel block, which by the experience of the author and her collaborators is well proved.

Thermocouples. Thermocouples are generally used for measuring the actual temperature of the furnace at all times and the departure of temperature between the sample investigated and the standard inert substance. As for the material of thermocouples, one can find in the literature dealing with d. t. a. examples for the application for various kinds of thermocouples. Application of thermocouples made of non-platinum metals is mainly advisable for relatively higher sensitivity. E. g. let us consider, taking the usual amounts of sample (0,2 to 0,5 g), at the endothermal peak of kaolinite not more than 10

to 15° C difference of temperature takes place between the sample and the inert substance. This difference of temperature produces in a platinum-platinum rhodium thermocouple a 100 μ V range tension. Highly sensitive measuring instruments are required for the observation of such a relatively low voltage. Consequently, many investigators prefer to employ thermocouples made of non-platinum metals as e. g. chromel (alumel or iron) constantan thermocouple, the voltage of which amounts to about the quintuple of that of platinum, and thus permits the use of simpler measuring instruments.

Thermocouples made of non-platinum metal, however, have a considerable defect, namely they are attacked by many samples, thereupon they become impure, and their voltage is very sensitive to impurities. The fault is increased even more by the fact, that only one junction of the differential thermocouple is placed in the sample, the other being in the inert substance, thus the impurities taking place at one of the junctions cause asymmetry, and pile up the defect. Another disadvantage of the thermocouples made of non-platinum metal consists of perceptible corrosion at about 1000°C. Taking all those facts into consideration, in spite of their lower sensitivity, application of platinum-platinum rhodium thermocouples seems to be more advantageous.

The most advantageous directives for the thickness of thermocouple wires are also given by experience. From the point of view of reproducibility it is important that the junctions of the thermocouples should always be placed in the same part of the hole of the sample holder. This requirement could be easier fulfilled by thick thermocouple wire which is more rigid and stable. Thick thermocouples, however, have on the one hand high thermal capacity, whereby sensitivity is decreased and, on the other hand, because of the higher thermal conductivity of large diameter thermocouple wires the thermal peaks become plain. The 0,3 mm diameter thermocouple wire has proved to be the most suitable, it fills both requirements better than any other.

As for the preparation of the junctions, one must be careful that they should not be soldered in a flame of too high temperature, for the loss which easily arises in consequence of evaporation of rhodium, can change voltage values. One has also to be careful that adventitious impurities should not get into the substance of the thermocouple during soldering, for e. g. the presence of 0,3% of iron impurity in platinum will cause about 4 mV (i. e. 400° C) difference at 1000°C (see W. GOEDECKE: *Über Thermoelemente und die Reproduzierbarkeit ihrer Daten*. Alberti, Hanau, 1931).

The junction balls should be as small as possible, for thereby one may increase sensitivity. It is important that the junction balls both placed in the sample and in the inert substance should be of equal size, otherwise certain difference of voltage takes place in consequence of the asymmetry. It is advisable to control by experiments whether accidental differences in the size of the two junction balls can cause any difference in voltage. The control is carried

out in the following way: After having placed both junctions in the inert substance, the furnace is heated, while the voltage of the differential thermocouple is being observed by the full sensitivity of the galvanometer. In case of symmetrical adjustment, the galvanometer does not show any deflection. If the galvanometer is deflected in any direction, one must find out whether this asymmetry takes place in the thermocouple or in any other part of the system (e. g. furnace). This problem is easy to solve. If the thermocouples are exchanged and the sense of the deflection becomes opposite thereby, the fault is to be found in the thermocouple. If the sense of deflection does not change by exchanging the thermocouples, the fault probably comes from unilateral radiation of the furnace which one can try to eliminate by axial swivelling of the furnace.

There are several requirements concerning the symmetry of thermocouples. If we consider that in the thermograms we want to observe peaks corresponding to as small differences of temperature as 1 to 2° C, that is to say that even as much as 1 μ V asymmetry should not be found in the thermocouple. In case of the thermocouple connection described below — which we have used for our investigations — we are able to compensate small voltage differences of the two thermocouples even by changing, as far as necessary, in the bridge circuit, the potentiometer compensating the internal resistance of the temperature measuring instrument.

Connection of thermocouples. As for the connection of thermocouples, temperature departures between the sample and the inert substance are most usually measured by two oppositely connected thermocouples, i. e. by differential thermocouples, the actual temperature being recently measured, mostly by a simple thermocouple sunk into the inert sample which is placed in a third hole. This solution is to be seen in fig. 12.

As for reasons expounded in the theoretical part of this paper, we have considered it advisable to measure actual temperatures in the sample itself, the connection of thermocouples has been carried out as follows. We have only two junctions on the thermocouple, one of them is placed in the sample, the other in the inert substance. The connection is carried out in such a way that we should be able, at the same time, to measure the actual temperatures of the sample, by the thermocouple placed in it. This was attainable by means of the bridge circuit which is to be seen in fig. 13. Thermocouple T_1 placed in the sample investigated (M) and thermocouple T_2 placed in the inert substance (I), coupled oppositely to each other, are measuring differences of temperature taking place between the sample and the inert substance, on galvanometer G_2 . Galvanometer G_2 connected with thermocouple T_1 is in turn measuring the actual temperature of the sample. The connection is made symmetrical by inserting as much ohm of resistance in the two wires of thermocouple T_2 as the internal resistance (R) of galvanometer G_1 .

LADDING and STURM [111] have increased the sensitivity of their apparatus by connecting several thermocouples in series.

Measuring instruments. There are different requirements concerning instruments measuring temperature on one hand and departures in temperature, on the other.

As for temperature measuring instruments, it is required that they should accurately follow the temperature of the sample investigated, therefore it is advisable to choose first rate laboratory instruments and not those of commercial quality and precision. Measuring instruments of 0,5% accuracy, equipped with a mirror scale are the most suitable for this purpose.

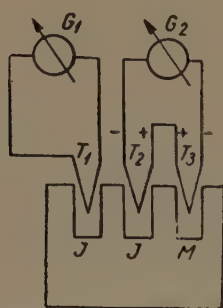


Fig. 12. Scheme of usual connection of thermocouples

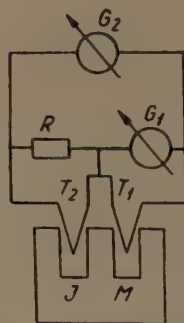


Fig. 13. Bridge circuit of thermocouples. (System Földvári-Vogl and Kliburszky, 44)

Taking into consideration that low voltages are to be measured, these instruments will point precisely, if their internal resistance is the multiple (possibly more than centuple) of the resistance of the thermocouples. We also have to take care, that instruments should be calibrated by including $2\ \Omega$ line resistance in their internal resistance. Consequently, if we are using such an apparatus, as much resistance is to be inserted in the circuit, as is necessary for bringing up the resistance of the thermocouples to $2\ \Omega$.

We have to mention here, that many investigators are keeping the cool points of the thermocouples in thermostat during d. t. a. investigations. Naturally, that is right in case of fully precise measurements, but at a 1000°C temperature difference, oscillations of 1 to 2°C do not generally affect the results of measurements.

The method applied in the institute of KURNAKOV gives a very agreeable solution: there the temperature of the sample is recorded by a mirror galvanometer, simultaneously to the difference in temperature. Hereby it is not necessary any more to mark the temperature in the record by special flashes at every 50 or 100°C .

In case of apparatuses functioning by electronical measuring instruments, there is simultaneous recording of the temperature of the sample, and of the temperature difference between the sample and the inert substance, respectively.

For the measurement of temperature differences, i. e. connected with the differential thermocouple, the most simple way is to apply a mirror galvanometer. For this purpose, an instrument of low internal resistance is to be chosen, for the lower the internal resistance of the galvanometer (most serviceable 2 to 50 Ω), the more sensitively are small differences in temperature observed. Consequently it is the most suitable to apply a mirror galvanometer of 10^{-8} A range of sensitivity and of 50 Ω internal resistance. A possibly vibrationless setting up of the galvanometer is required too. The most suitable solution for recording the light signal, consists in recording the image of the heater filament in the mirror of the galvanometer by the condenser of the projector lamp, the image of the aperture taking place in front of the condenser of the projector lamp which in turn is recorded on the record chart by the lense placed before the mirror of the galvanometer.

In case of galvanometers of the aforesaid sensitivity, it is quite sufficient to place the recorder at a distance of 50 to 100 cm from the galvanometer. Naturally, the focal distance of the lense placed in front of the galvanometer is to be changed at the same rate.

The mirror galvanometer is completed by a sensitivity controller, by which, in a reproducible way, the sensitivity of the galvanometer is changeable. Ayrton-connection of the sensitivity controller is advisable in order to insure the constancy of a period of oscillation of the galvanometer, furthermore, the sensitivity controller must be staggered, whereby every kind of deflection can be recorded, from the smallest quartz peak to the largest calcite peak.

In electronic recording equipments (e. g. Speedomax) all those requirements are obviously dispensable, because of the high input resistance of electronic sets. Electronic recorders also have the advantage that, as recording is not carried out on photogenic paper, but by a chart-recording instrument, every partial feature of the process is immediately observable. Although these sets automatically, control themselves, the use of such equipments depends on more conditions, than that of the mirror galvanometers.

Recording equipment. The simplest way of recording consists in projecting the strong light signal reflected from the mirror of the galvanometer to photosensitive paper, through a 0,1 to 0,2 mm aperture. The photosensitive paper is fixed to a cylinder rotated by clockwork. The chartspeed must be brought into accord with the length of the thermal investigation. It has proved very serviceable in practice to place the whole recording system, i. e. the galvanometer and the recording cylinder in a light-tight box. This procedure permits the carrying out of such investigations by daylight. In such a case it is advisable to distribute the light by a mirror placed at 45° angle in the way of the light, and to project

it to the opaque scale of the cover of the box, in order to control the movement of light during determination. The suitable width of the paper is 10 to 12 cm, electrocardiograph charts are very useful for this purpose.

In electronic sets, recording is carried out by a pen arm, mostly by multi-colour pencils, permitting simultaneous recording of several parallel determinations.

Apparatuses constructed by the author and her collaborators

In our practice, up till now, two types of apparatus have proved to be most useful. Both were constructed by us. One of these d. t. a. equipments is constructed on the basis of the theoretical considerations, which have been pointed out hitherto, and can be used at the usual $10^{\circ}\text{C}/\text{minute}$ heating rate. More than 1500 investigations have been carried out by this apparatus. Much higher heating rate can be obtained by the other apparatus, a rate of $80^{\circ}\text{C}/\text{minute}$ has proved to be the most suitable.

1. *Apparatus working at $10^{\circ}\text{C}/\text{minute}$ heating rate.* Like every other d. t. a. apparatus, this set consists of three main parts: 1. furnace and equipment controlling the heating current of the furnace, 2. sample holder block with holes for the sample investigated and the inert substance, 3. thermocouples for measuring the temperature and temperature departure, with measuring instruments belonging to same. The set is completed by an equipment for automatic photographical recording of the light signal.

As for the construction of the furnace, the aforesaid view-points have been taken into consideration. Uniform controlling of the specified rise in temperature is not easily insured, unless furnace temperature rapidly follows the changes of the controller. It is obtainable by decreasing the thermal capacity of the furnace. For this purpose, the heating wire insulated by porcelain beads have been wound, contrary to the usual way, on the inside surface of the ceramic tube. Thereby it was attained that the heating wire radiated directly on to the sample holder block, and in not more than 1 or 2 minutes the control of the furnace current was followed by a change of temperature taking place in the sample holder block. Thus we succeeded in keeping the prescribed time-pattern during the whole length of heating, within about 10°C of deviation. This heating body shape has a considerable advantage, namely the temperature gradient between heating wire and sample holder block is low, about 50 to 60°C per cm. This fact implies a practical advantage, namely it is not necessary to overheat the heating wire in order to attain the temperature required in the block, consequently a longer duration of the furnace is insured.

The inside diameter of the ceramic tube of the furnace used in our investigations is about 70 mm, the diameter of our "Kanthal A" heating wire 0,7 mm, maximum input power 450 W. Before beginning the measurements, the

furnace is perpendicularly covered over the sample holder block, in such a way that the block is placed in the middle of the heating space. Uniform heating of the furnace is insured by means of a resistor which is variable by a synchronous clockwork.

The sample holder block is a cylinder made of chromous and nickelous heat resistant steel, 30 mm in diameter and 20 mm in height. The drawings of the block is to be seen in fig. 11.

Pt/PtRh thermocouples have been used as thermoelements, in a connection to be seen in fig. 13.

As for the positioning and fastening of the block and the thermocouples, we have taken great care of the following: on one hand the requirement of thermal symmetry must be fulfilled, on the other hand reproducibility of the

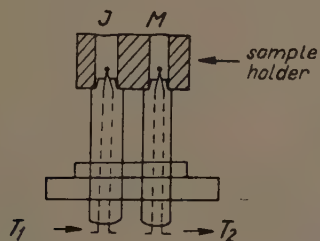


Fig. 14. Positioning of sample holder

fastening is to be insured, finally by fastening the sample holder block, one must not take any further element inside the furnace whereby the thermal inertia of the system would be increased. The sample holder is fastened by the insulating porcelains of thermocouples T_1 and T_2 , which in turn are fixed outside the heating space of the furnace, protected against thermal corrosion (see fig. 14).

By setting the thermocouple porcelains into the holes of the sample holder, the position of the thermocouples is always central, which is rather important for the reproducibility of the measurements. This solution has a further advantage, namely deformations taking place in the sample holder in consequence of heating have no effect upon the measurement, in consequence of the rotation symmetry of the system.

Our measuring instruments fill the above exposed requirements (mirror-scale temperature measuring instrument and mirror galvanometer).

Our recording equipment has been constructed in the usual way. It is a cylinder driven by motor, photosensitive paper being fixed on the cylinder. The photosensitive paper records the light signal reflected from the mirror of the galvanometer.

2. Our "rapid" d. t. a. apparatus. This apparatus has been experimentally worked out in 1955 and our first results published [84, 45]. Since then a modified

type of our apparatus to carry out serial investigation has been used for some months at the Hungarian Geological Institute. A photograph of the apparatus is to be seen in fig. 15 where informations are also given on the measures of the component parts.

The apparatus described in *Acta Geologica* [84] has exclusively served in principle to decide, whether any change in the shape of d. t. a. curve was caused by rapid heating. As initial experiments have shown, that no considerable

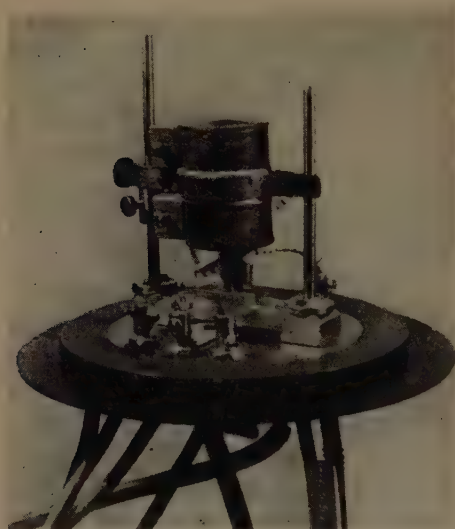


Fig. 15. "Rapid" d. t. a. apparatus (during measurement)



Fig. 16. "Rapid" d. t. a. apparatus, the furnace is lifted up from the sample holder jacks (after measuring)

change takes place in the position of the curves, even by decoupling heating velocity, and in order to adapt it to practice, we have reconstructed our apparatus. In our paper quoted above we have employed a horizontal furnace and the heated substance decomposed in a totally closed space. As the escape of reaction products has thus become difficult, the shape of the thermograms became a little plainer. A further disadvantage consisted in the fact that it was difficult to eliminate from the apparatus the substance coked in many cases, after having carried out the investigation. Therefore our apparatus has been reconstructed in the following way: we have taken a vertical furnace in which uniform distribution of temperature is insured by a thick-walled quartz tube. This quartz tube of 14 mm in caliber is in fact the inside surface of the furnace. A thread of 2 mm pitch is cut on the outside surface of the quartz tube, holding the 1,4 mm thick "Kanthal A" heating wire. The total resistance

of the heating wire is ca. 1Ω . The outside of the furnace consists of a brass jack 60 mm long and 50 mm in diameter, which at the same time holds the insulated current lead. Between the brass coating of the furnace and the heating wire there is an asbestos heat insulation. The body of the furnace is held by a clamp permitting axial swivelling of the furnace in order to compensate possible

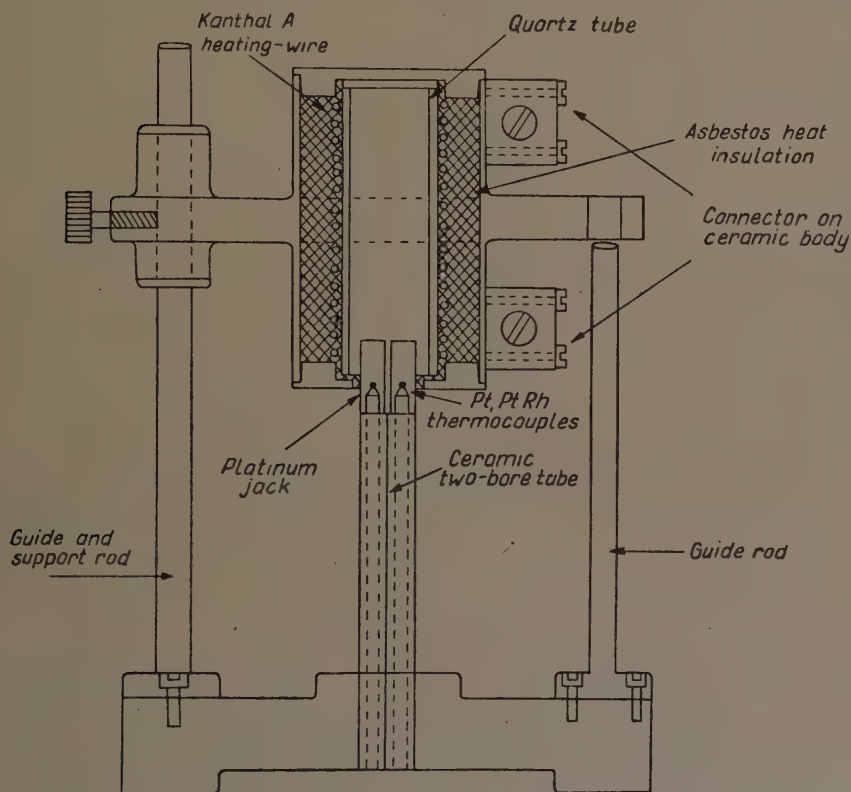


Fig. 17. Drawing of "rapid" d. t. a. apparatus

thermal asymmetries. The clamp holding the furnace is guided by a column of 6 mm in diameter on which the furnace can be slipped up and down. The other end of the shackle supporting the furnace is forked, and it is guided by another 6 mm column, which at any time permits the replacement of the furnace in the same position, and fasten it there.

The sample holder consists of two nickel jacks, held by the two-bore porcelain insulators of the thermocouples. Those porcelain insulators are 6 mm in diameter and fastened outside the heating space of the furnace. The sample holder jacks are made of 0,3 mm thick nickel plate, 5 mm in diameter and 15 mm in height. The sample investigated of ca. 200 mg and the same amount of inert substance are placed in the respective jacks.

As thermocouple-wire, Pt/PtRh is, here too, applied, the connection of the thermocouples is the same as in our above described apparatus.

The measuring instruments may be the same as in our previous set, on condition that quick-swinging galvanometer is to be used for the observation of temperature differences (time constant 0,1 sec).

As for the recording equipment, we must only mention, that the chart-speed must be brought into accord with the rapidity of determination, that

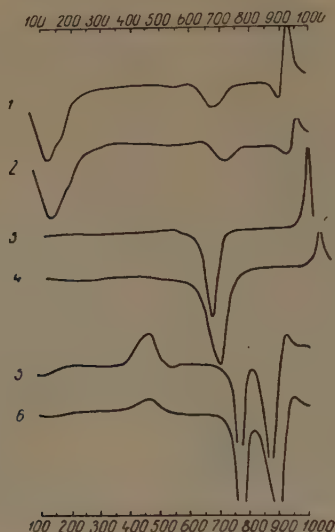


Fig. 18. Comparison of d. t. a. curves made by "slow" and "rapid" apparatuses

1. Bentonite, Little Rock, Arkansas (by "low" apparatus)
2. Bentonite, Little Rock, Arkansas (by "rapid" apparatus)
3. Dickite, Ouray, Colorado (by "slow" apparatus)
4. Dickite, Ouray, Colorado (by "rapid" apparatus)
5. Pyritiferous dolomite, Fenyőfő (by "slow" apparatus)
6. Pyritiferous dolomite, Fenyőfő (by "rapid" apparatus)

means a chart-speed of ca. 2 cm/minute ; taking the measures of our recorder into consideration.

Naturally, a higher chart-speed requires a more intense recorder lamp (ca. 5 to 6 W).

Figs. 15, 16, and 17 show a scale-drawing and photographs of our "rapid" apparatus. In one of the photographs the furnace is covered over thermocouples, ready for measuring, the other photography was taken at a cooling phase, after having removed the furnace from the thermocouples and the sample holder jacks.

In fig. 18 thermograms of some substances are shown, parallely taken by our "slow" and "rapid" apparatuses. As is to be seen, the curves are in perfect

accordance, there is but one difference, namely the peaks of d. t. a. curves taken by the "rapid" apparatus are shifted by 20 to 30° C towards higher temperatures. Naturally, this fact is not disturbing, if standard samples are investigated under similar conditions.

However, there is a considerable difference in sensitivity between the determinations carried out by the two apparatuses. In spite of the fact that the same mirror galvanometer and the same Pt/PtRh thermocouples have been used in both sets, furthermore the resistance controlling the sensitivity of the galvanometer has been doubled in the "rapid" apparatus, nevertheless in the case of our "slow" apparatus we have obtained, by measuring off ca. 0,4 to 0,5 g, peak areas of as large an extension as in the case of the "rapid" apparatus by measuring off 0,10 to 0,15 g. This means briefly, that the sensitivity of our "rapid" apparatus is about eight times higher. Consequently it must, again, be emphasized that, in quantitative determinations, reproducibility of heating of the furnace is quite important, in order to obtain comparable peak areas. As for the rise of sensitivity, we have to mention, that it is conspicuous particularly in endothermal processes.

Summing up our experiences, we have pointed out that our "rapid" apparatus was quite serviceable for every kind of qualitative analysis and even quantitative analyses of informative nature, the apparatus of lower heating rate being necessary only for investigations requiring higher accuracy.

II. SPECIAL PART

In this part we have exposed d. t. a. curves of several minerals. They have been compiled, partly by taking into consideration the literature referring hereto, partly on the basis of data obtained from occurrences in this country. In many cases, we are also mentioning curves of the mixtures of those minerals which in nature often occur beside each other. In most cases we have been able to interpret the peaks of the thermograms. We also point out circumstances in certain cases having affect on the shape of the thermograms.

Minerals are treated in the order of mineral groups, the respective classes have been systematized according to the order established by SZÁDECZKY and applied by KOCH and SZTRÓKAY (SZÁDECZKY: *Rendszeres ásványtan*, Miskolc 1950, KOCH and SZTRÓKAY: *Ásványtan*, Budapest 1955). Naturally, we are treating only those mineral groups, and within the groups only those minerals, which have in fact characteristic d. t. a. curves, or rather the thermogram whereof is known.

D. t. a. curves taken by different sensitivities and published on different scales by various authors have been redrawn on a uniform scale, without thereby carrying out any substantial change.

1. Native elements

The determination of native elements by physical and chemical methods is generally an easy task, consequently d. t. a. is scarcely used for this purpose. In principle, it is obviously possible to apply d. t. a. investigation to the problem, if the change in state or inversion point of modification of a given element takes place within those limits of temperature which are generally suitable for d. t. a. As physical constants of those elements are known and accessible to everybody, anybody can decide on the possibilities of application from case to case.

2. Sulfides

There are relatively scanty data in literature on d. t. a. of sulfides. In fact, pyrite is the sole sulfide mineral, the curve of which is very often seen, because it frequently occurs as impurity of clays and of other rocks too. The thermogram of pyrite is characterized by an exothermal peak taking place between 400 and 450° C, in consequence of oxidation of the pyrite. The shape of that exothermal peak is, however, very capricious and changeable, sometimes it is even double, which is due to the particle size of pyrite but perhaps to differences in modification too. According to J. KONTA the oxidation of melnikovite takes place at 415° C, that of marcasite at 440° C, that of well crystallized pyrite at 460 to 470° C. Bond strength between Fe and S is relatively the highest in pyrite.

If the identification of some mineral is troubled by the peak of pyrite, it is possible to eliminate this peak by carrying out the determination in an inert atmosphere. That is shown by curve No. 7 in plate I/a. One has to take into consideration, that some organic substances can always be present in the sample and the oxidation of that material possibly takes place in temperature ranges similar to those of the oxidation of pyrite and affined sulfides. Although the shape of the curve reveals the difference — for a well-skilled investigator — between the two possibilities, namely that the oxidation of an organic substance generally produces a wider, more spacious exothermal peak than that of pyrite, the determination is, however to be carried out with the utmost care.

Besides pyrite, we present a curve of sphalerite, according to KAUFMAN and DILLING [78] (fig. 6 in plate I). Sphalerite alters at 1020° C into hexagonal wurtzite, that reaction, however, has been overlapped by the exothermal peak representing violent oxidation of this mineral in the same temperature range, as is to be seen in the figure.

As has been mentioned above, the shape of d. t. a. curves of pyrite — and generally of sulfides — becomes quite different when investigations are performed in an inert atmosphere, e. g. in nitrogen. J. E. HILLER and K. PROBSTHAIN

carried out adequate modifications in the apparatus for sulfide investigations, or rather they chose the parts of the apparatus in such a way, that the risk of corrosion taking place during decomposition or fusion of sulfides should be as low as possible. They used Ni/CrNi thermocouples 0,7 mm in diameter, and inserted a Pythagorean tube in order to prevent corrosion. Although sensitivity was thus a little decreased, it proved to be sufficient for their investigation. Similarly, because of risk of corrosion, the use of metallic sample holder blocks is to be avoided, in their stead we may choose ceramic or any other non-metallic, suitable substance.

The results of the investigations of HILLER and PROBSTHAIN are presented in plate I/b.

Pyrite from 616° C on shows a large endothermal peak at which the decomposition $\text{FeS}_2 \rightarrow \text{FeS} + \text{S}$ takes place. The slow endothermal inclination to be seen above 800° C represents the splitting-off of residual S. The interpretation of the endothermal peak to be seen in the d. t. a. curve of chalcopyrite from 544° C on, is still not reassuring. In the thermogram of covelline an endothermal peak starts at 448° C, which represents the following process: $2 \text{CuS} \rightarrow \text{Cu}_2\text{S} + \text{S}$. If heating of covelline is not performed by excluding air, the aforesaid endothermal peak is followed at 554° C by another endothermal peak, where the following alteration takes place: $\text{Cu}_2\text{S} + 2 \text{Cu}_2\text{O} \rightarrow 6 \text{Cu} + \text{SO}_2$. In case of antimonite, the peak starting at 484° C represents the sublimation of antimonite. In the d. t. a. curve of argentite, we may see a peak starting at 173° C and marking an alteration in modification. From 800° C on, the substance fuses during decomposition, which is represented by an endothermal peak in the thermogram.

3. Oxides and hydroxides

In d. t. a. curves of minerals belonging to this group, peaks may be produced by the following processes: dehydration of hydroxides, formation of stable oxide at high temperature in the oxide minerals of elements of varying valence, alterations in modification.

a) *Silicon dioxide* (SiO_2)

It is known that SiO_2 has three important homotypic modifications: quartz, tridymite, and cristobalite, all three having two enantiotropic modifications: α and β . The constitutional diagram of SiO_2 -modifications indicates that β quartz is stable from ordinary temperature up to 573° C, α quartz from 573° C to 870° C, α tridymite from 870° C to 1470° C, α cristobalite from 1470° C

to 1713° C. For reasons of d. t. a. technique, only the alterations taking place at 573° C and 870° C are to be taken into consideration, in some cases one may take into account the alteration of supercooled tridymite or cristobalite systems, taking place at 130° C and between 180 and 270° C.

In d. t. a. practice, β quartz \rightarrow α quartz inversion taking place at 573° C is the most widely known. The process implies heat absorption, consequently it is indicated by an endothermal peak. The inversion heat, however, is relatively very low, the peak area is therefore very small. The process takes place very rapidly, the presence of quartz being indicated by a small, sharp peak in the d. t. a. curve at 573° C. As the inversion in question is a reversible process, it is possible to detect the quartz peak, even if there is some other mineral, the peak of which appears in the same range of temperature and overlaps the small quartz peak. Namely, in that case we let the sample cool after having carried out d. t. a., and then we reanalyse the cooled off sample. As the disturbing peaks are generally results of irreversible processes, they do not appear any more during the second heating, thus the second thermogram only shows the quartz peak.

According to the investigations of G. T. FAUST [37] the peak indicating the inversion of quartz is independent of the conditions of the formation of quartz crystal, therefore as a process of quite reliable temperature, it is proposed by FAUST for the calibration of d. t. a. sets. However, we should mention that TUTTLE and KEITH [165] have recently pointed out, that $\alpha \rightarrow \beta$ inversion of quartz was a function of formation temperature, consequently, in certain cases one can even find as much as 38° C difference between inversion temperatures.

There are far less data on α quartz \rightarrow α tridymite inversion taking place at 870° C, in the literature referring to d. t. a. FAUST does not mention that peak, R. E. GRIM and R. A. ROWLAND [62] in turn point out that they were not able to detect it in their d. t. a. curves. The author of this paper and her collaborators have observed that generally the peak of 870° C did not appear in the quartz curve, nevertheless in certain cases, as e. g. in that of a rock crystal of Máramaros, a small endothermal band is definitely observable at about 870° C.

In plate II, the curve of Máramaros rock crystal is presented, in addition to some quartz curves taken over from the literature, furthermore examples of the presence of a quartz peak beside other peaks are given. In this case, a very small quartz peak appears in the upward tending side of kaolinite peak. As has been mentioned above this detection is only then reliable, if the presence of quartz has been detected by repeated heating, too.

There are no data on further inversions in modification of quartz in the literature referring to d. t. a.

It is obvious, that this method is not adequate for the detection of amorphous silicon dioxide.

b) *Manganic oxides*

The thermogram of *pyrolusite* (and *polianite*) (MnO_2) shows two endothermal peaks, the first having a peak maximum between 640 and 670°C, the second one between 960 and 1050°C. At the first peak MnO_2 becomes $\beta \text{Mn}_2\text{O}_3$, at the second peak $\text{Mn}^{\text{II}}\text{Mn}_2^{\text{III}}\text{O}_4$ (*hausmannite*) is formed from Mn_2O_3 . Both processes are irreversible.

KULP and PERFETTI [97] mention a rhombic variety of *pyrolusite*, namely *ramsdellite*, the curve of which differs from that of *pyrolusite* by only a small exothermal peak appearing at about 500°C, the inversion of the *ramsdellite* into *pyrolusite* takes place there, afterwards the substance, and consequently its curve, are totally identical with *pyrolusite*.

According to KULP and PERFETTI, *hausmannite* $\text{Mn}^{\text{II}}\text{Mn}_2^{\text{III}}\text{O}_4$ does not show any process consequent to heat change up to 1000°C. According to RODE [137] on the other hand, natural or α *hausmannite* alters at about 890 to 960°C into β *hausmannite* by an irreversible process, the latter altering by further heating between 1180 to 1220°C into γ similarly modification in the course of an endothermal process, which this time is reversible.

Braunite $(\text{Mn}, \text{Si})_2\text{O}_3$ is a complex oxide or, according to other authors, an oxide silicate. According to KULP and PERFETTI the thermogram of *braunite* does not show any peak up to 1000°C, according to RODE the α *braunite* $\rightarrow \beta$ *braunite* inversion is marked by an endothermal peak in the curve of *braunite* between 1030 and 1100°C.

Thermograms of the oxidic minerals of manganese are not yet sufficiently congruent, therefore it seemed to be advisable to investigate laboratory-made artificial manganese minerals too [48]. In plate III we present d. t. a. curves of some artificial manganic oxides which were made by Gy. GRASSELLY [57]. As is to be seen, there is only one difference between the curves of artificial and natural manganic oxides, namely in the case of artificial samples the peaks appear at a somewhat lower temperature. This is obviously due to the finer particle size of the artificial mineral. In the curve of artificial *hausmannite* (curve 8, plate III) a plain endothermal peak appears between 900 and 1000°C which may correspond to the inversion into β *hausmannite* mentioned by RODE. The peak appearing at about 980°C in the d. t. a. curve of artificial Mn_2O_3 (called *kurnakite* by RODE) indicates the inversion of Mn_2O_3 into *hausmannite*.

As various manganic oxides can occur in nature beside each other, we present in table IV thermograms of mixtures of manganic oxides, in order to facilitate evaluation of d. t. a. curves.

c) *Manganic oxy-hydroxide, manganite, $\text{MnO}(\text{OH})$*

In the thermogram of *manganite* an endothermal peak appears between 350 and 400°C, where manganite alters into Mn_2O_3 . If heating is continued, Mn_2O_3 produced in the above-mentioned way alters into hausmannite between 950 and 980°C (as it has been seen) and a second endothermal peak appears in the curve of manganite (see curve 1, plate IV).

d) *Iron hydroxides*

Goethite, as α modification and *lepidocrocite* as β modification of FeO OH give very similar d. t. a. curves. Both minerals lose their hydroxide radical between 300 and 400° C and alter into Fe_2O_3 , but they differ in peak temperature since the peak of goethite appears between 370,400° C, while that of lepidocrocite at about 30 to 40° lower. This difference in decomposition temperature may be interpreted by differences in crystal structure (BRAGG) between the two minerals. The difference in the bond shape of H atom here plays an important part. In goethite H appears as cation between O atoms, while lepidocrocite contains independent OH groups. The latter is a somewhat less stable structure, consequently its decomposition takes place more rapidly. There is still another difference in the thermograms of the two minerals, after the respective endothermal peaks. The curve of goethite returns to its base line after the peak and it does not show any further peak, while in case of lepidocrocite a small exothermal peak appears over 400° C. That is while the decomposition of goethite directly produces α hematite, the result of decomposition of lepidocrocite is γ hematite, which in turn is transformed, over 400° C, into α hematite, in the course of an endothermal process.

Very frequently, it happens that lepidocrocite and goethite in nature occur beside each other. In such a case, as is to be seen in curve 4 of plate IV, a well defined double peak appears between 300 and 400° C. If there is a too large amount of goethite, the development of the small exothermal peak of lepidocrocite can be hindered by the endothermal peak of goethite.

Sometimes it is difficult to detect manganite and limonite minerals from each other. According to our experience, at the detection of such minerals beside goethite some difficulties are really to be considered, although the second peak of manganite may present a certain basis. However, detection is possible in the presence of lepidocrocite, the peaks are distant enough and, as is shown by curve 8 in plate IV, the two peaks appear separately in the case of an artificial mixture of manganite-lepidocrocite.

e) *Magnesium hydroxide, brucite, $\text{Mg}(\text{OH})_2$*

At ca. 450° C, the thermogram shows an endothermal peak which is due to dehydration; the result of dehydration is periclase (MgO). The curve of brucite is to be seen in plate V (curves 1 and 2).

f) *Aluminium hydroxides and oxy-hydroxides*

Hydrargillite (gibbsite) $\gamma \text{Al}(\text{OH})_3$. An endothermal peak representing dehydration appears at ca. 350° C. Neither the data referring hereto, nor experience are perfectly unequivocal, concerning the result of this dehydration of hydrargillite. According to a great number of investigators, e. g. BRAGG, hydrargillite alters at first into boehmite, and the latter, in a second step, into $\gamma \text{Al}_2\text{O}_3$. As a matter of fact, many hydrargillite curves show a second, smaller endothermal peak at ca. 540° C which may represent the dehydration of boehmite. However, in the literature one can find many hydrargillite curves only showing the first peak, while the second peak is hardly discernible or not visible at all. E. g. such a hydrargillite curve has been obtained by the author from a hydrargillite sample of a thermal source of Istria (Dalmatia) (see curve 3 in plate V). Consequently, it is questionable why the boehmite peak does not appear in every case, if it is true that hydrargillite decomposes first into boehmite, and on the other hand even if the second (boehmite) peak appears, whether it is due to the boehmite impurity present originally in the hydrargillite sample. The same question was raised in two Hungarian papers. K. SASVÁRI and A. HEGEDŰS [148] tempered natural hydrargillite at 300° C during an hour and thereafter they detected boehmite in the sample by X-ray investigation, at the same time they could not observe the interference ring of $\gamma \text{Al}_2\text{O}_3$. They came to the conclusion, that natural hydrargillite altered into Al_2O_3 through boehmite. However, the boehmite produced in this way, and the amorphous Al_2O_3 possibly present, went on decomposing after a further small rise in temperature, consequently the d. t. a. curve does not show any boehmite peak in the expected place. L. ERDEY and F. PAULIK [33] obtained three endothermal peaks in the thermogram of an artificial pure hydrargillite (curve 4 in plate V): a small peak at 240° C, a large peak at 310° C, and again a small one at 525° C, they interpreted the presence of the small peaks by gradual dehydration. On the basis of the ERDEY—PAULIK-curve, however, it is improbable that hydrargillite would decompose by completely altering into boehmite after 350° C, which in turn goes on altering at ca. 540° C, for the peaks of hydrargillite and boehmite are disproportionate. According to DE BOER, FORTUIN and STEGGERDA both hydrargillite and bayerite can occur in two different forms [28]. Hydrargillite 1 and bayerite 1 directly alter into $\gamma \text{Al}_2\text{O}_3$ at the endothermal peak taking

place at about 250° C, while the dehydration of hydrargillite 2 and bayerite 2 at about 250° C results in a mixture of boehmite and γ Al_2O_3 . The problem can not be considered as concluded; Hungarian investigators (SASVÁRI, GEDEON) are also continuing their investigations in this matter.

SASVÁRI and his collaborator [149] consider the problem of hydrargillite decomposition, on the basis of recently published considerations concerning its crystal structure, as follows.

By some of their own experiments they also support the observation of DE BOER and his collaborators according to which the process of decomposition of hydrargillite and boehmite depends on the particle size of the samples. Namely, in case of large particle size, the water released inside the particles produces a high hydrothermal pressure, which lasts until the particles disaggregate on the effect of internal pressure. Under the influence of such a hydrothermal pressure, decomposition takes place through boehmite. On the other hand, in case of small particle size, both bayerite and hydrargillite, directly decompose into the dehydrated form, without any hydrothermal effect.

Hydrargillite is an important mineral of many bauxites. As for Hungarian bauxites, it is particularly dominant in those of Iszkaszentgyörgy and Halimba [41]. Curves 5 and 6 of plate V have been recorded from bauxite samples of Iszkaszentgyörgy and Halimba respectively, the peaks of kaolinite beside those of hydrargillite are to be observed in each curve.

Bayerite β $\text{Al}(\text{OH})_3$, is an artificial aluminium hydroxide, its thermogram shows, according to KAUFMANN and DILLING, a double endothermal peak, the first peak appearing at ca. 270° C, the second, larger than the former one at about 330° C. At about 550° C there is only a small band (curve 7, plate V).

Diaspore α $\text{AlO}(\text{OH})$, during heating loses its OH content over 500° C. In its thermal curve, an endothermal peak taking place between 530 and 540° C represents that process. There is no other characteristic peak in the curve of diaspore (curve 1, plate VI).

Beside hydrargillite, both diaspore and boehmite are very important bauxite minerals. Besides these kaolinite, and possibly also limonite may be present, the detection of the latter minerals is also possible by d. t. a. Consequently d. t. a. has proved to be a very suitable, rapid method for the detection of the most important bauxite minerals, except for hematite, and it made quantitative determinations possible too. In some cases, however, evaluation of d. t. a. curves of bauxites is to be carried out with the utmost care, for without adequate experience one can give erroneous determinations. E. g. lepidocrocite is well traceable beside hydrargillite (curve 3 in plate VI) but in case of simultaneous presence of goethite and hydrargillite the peaks may disturb each other considerably. Two other minerals disturbing each other are boehmite and kaolinite, for there is but some 20° C difference between their peaks. Although double peaks generally show the simultaneous presence of

two minerals (see curve 4 in plate VI), in case of quantitative determination the peak area is only measurable by the "compensating" method shown above. The peaks of diaspore and kaolinite are well defined, as is to be seen in curve 5 of plate VI. The bauxite of Nézsa represented in plate VI contains diaspore and kaolinite. The d. t. a. curve of the clayey bauxite of Gánt, shows between 300 and 400° C the peaks of lepidocrocite and hydrargillite, thereafter between 500 and 600° C those of boehmite and kaolinite. From the d. t. a. curve of the bauxite sample of Nagynémetegyháza, one may conclude to the presence of hydrargillite, boehmite and kaolinite (curve 6 in plate VI).

It is probable that, within the domain of practical investigations, d. t. a. as a rapid method of industrial material testing, will be generally applied, because it may be rapidly carried out by relatively simple means, and with sufficient accuracy, even in case of bauxite minerals and of kaolinite generally present, including quantitative determinations. This prompted S. B. HENDRICKS and his collaborators [72] to construct a portable d. t. a. apparatus which could be used in the field of bauxite investigations, too.

4. Silicates

The examination of silicates in petrology and geochemistry is of great importance, as silicate minerals play a dominant part in the earth's crust. Silicate minerals, and among these, principally clay minerals, represent one of the most important domains where d. t. a. is applicable. As for clay mineral investigations, d. t. a. has been given an important role, as the application of the usual methods for mineralogical investigation encounters some difficulties, in consequence of the small particle size of these minerals. Naturally, even among clay minerals, only those may be taken into consideration for d. t. a., which during heating undergo alterations depending on the measurable change in heat content. Thus, first of all, one may consider minerals containing OH radical in their structure, or undergoing some characteristic alteration in modification, at certain temperatures. D. t. a. curves of many silicate minerals, besides clay minerals are known, but perhaps it is the very territory where the possibilities of this method are not at all exploited, and still much is to be achieved.

When we are dealing with d. t. a. investigations of silicates, we have to deviate from the order of succession established by SZÁDECZKY and employed by KOCH and SZTRÓKAY, for taking into consideration the special importance of clay minerals, they must be treated apart. Before dealing with clay minerals we shall sum up the results of d. t. a. obtained up to now, concerning other silicate minerals. We shall omit from this synthesis all investigations which are doubtful, or which contain obviously erroneous statements in some cases, for these investigations may possibly lead to further errors and contradictions.

a) *Tourmalines*

The most important informations on the thermal behaviour of minerals belonging to this group are given in a paper by C. KURYLENKO [103]. On the basis of the investigations of KURYLENKO, a common property of tourmalines of different types and localities, consists in losing their water-content at about 145°C for the most part, but most samples show two further small peaks representing the escape of residual water: the first peak appears between 430 and 480°C, the second one at 770°C. However, every kind of tourmaline seems to have a general characterization by a large endothermal peak which appears between 950 and 970°C and which is to be attributed, according to KURYLENKO, to the loss of B_2O_3 content of the tourmaline. The first three curves of plate VII have been recorded from black tourmalines, they are sufficiently concordant curves, showing rather equal development of all three of the peaks resulting from dehydration and of a high temperature endothermal peak. Curve 4 has been recorded from a sample of black tourmaline (of Madagascar) which, according to the author, was not an intact sample but an altered one, its peaks resulting from dehydration, appear anomalously. Sample No. 5 is a colourless tourmaline of Elba, it shows a d. t. a. curve which is very similar to the three former ones, except that the two larger peaks representing dehydration do not appear. Curve No. 6 represents a tourmaline of a dravite type, of high Mg content, this curve is different from the others as well as of thermogram No. 7, which was recorded from a rubellite sample.

On the basis of all these, one may point out, that adequate criticism is absolutely necessary for the determination of tourmalines by d. t. a., just because of the great variety of these minerals. On the other hand, d. t. a. gives a possibility for fuller determination of several sorts of tourmalines.

However, we have to remark here, that it is questionable whether KURYLENKO was right in pointing out that at 145°C the tourmalines lose most part of their constitutional water. The data on the thermal decomposition of tourmalines are not to be considered as decisive.

b) *Amphiboles*

Amphiboles containing OH, lose the OH radical at different temperatures in function of the bond strength of it. D. t. a. curves of the different members of the amphibole group, moreover, by quantitative evaluation of the curves, respective degrees of change in heat content depending on dehydration, are here given on the basis of a paper by M. WITTELS [177]. Plates VIII/a and VIII/b present the d. t. a. curves of WITTELS, recorded from different sorts of amphiboles. These curves, and all kinds of amphibole, are characterized by

the fact that they lose their OH groups between 925 and 1125°C, the crystal structure of amphibole disaggregating at the same time. In the curves of WITTELS, this process is represented by an endothermal peak marked in every case with „y”. WITTELS has given the curves only over 600°C, for he observed no thermal process in any sample under 600°C. Further peaks appearing before that marked with „y” represent alterations in modification in case of the members belonging to the group of Mg content, and oxidation of ferrous iron in case of ferrous samples.

c) *Sepiolite*

On the basis of its structure, sepiolite is to be classed among the amphibole-like minerals but, together with attapulgite, they are often classed among the clay minerals s. str., too. Its thermal curve was first determined by S. CAILLÈRE [21], later investigators obtained similar curves. The first endothermal peak appears at ca. 150°C, representing the escape of adsorptive water. This is followed by a second, smaller endothermal peak at ca. 440°C according to CAILLÈRE, or rather under 400°C, according to other authors. This peak representing the escape of OH also causes some structural changes in the sepiolite. A further endothermal peak appearing at 750°C shows the total destruction of the lattice, this one is immediately followed, over 800°C, by a sharp endothermal peak representing the heat released at the formation of a new crystal phase.

Attapulgite (paligorskite) shows a d. t. a. curve very similar to that of sepiolite, but the first endothermal peak of attapulgite is double, the second, smaller endothermal peak appears at a somewhat higher temperature.

Plates IX and X show d. t. a. curves of samples of sepiolite and attapulgite, published by various authors. In curve No. 3 of plate X, a quartz peak is to be seen, after the endothermal peak appearing at about 500°C.

d) *Serpentine minerals*

According to our view-points it is advisable to mention, in this part of our paper, the thermal investigation of serpentine minerals too, although this order is not quite logical on the basis of the structure of these minerals.

The thermal behaviour of serpentinites has been thoroughly studied by S. CAILLÈRE [21]. On the basis of d. t. a. curves, he has divided serpentine minerals into two groups. Thermograms of the first group are characterized by an endothermal peak appearing at ca. 650°C in consequence of dehydration, this peak being followed by an exothermal peak between 750 and 825°C. CAILLÈRE has proposed to name this group α antigorite. In the thermal curves of the other group, the endothermal peak does not appear, he has named this group

β antigorite. In plate XI three asbestos minerals are presented, according to CAILLÈRE, one of these minerals belonging to the α and two to the β antigorite group, further on we see d. t. a. curves of two serpentinite samples according to KAUFMANN and DILLING [78], the latter ones representing both groups established by CAILLÈRE. In curve No. 3 there appears over 450°C the peak of brucite, besides that of chrysotile. It is of interest to mention that N. S. KURNAKOV and V. V. CHERNYCH [101] have obtained substantially quite similar thermal curves of serpentine minerals as early as 1926. The two last curves of plate XI show Hungarian serpentine occurrences.

B. NAGY and FAUST [120] have recently dealt with d. t. a. investigation of serpentine minerals too. They have pointed out, that the serpentines consisted either of chrysotile or of antigorite or of a natural mixture of both. On the basis of their d. t. a. curves, it becomes obvious, that the α antigorite of CAILLÈRE corresponds to chrysotile, β antigorite to antigorite.

e) *Micas and mica-like minerals*

Talc-group. Talc. Its thermal curve is shown in plate XII according to R. E. GRIM and R. A. ROWLAND [62] but quite similar curves have been obtained by ORCEL, NORTON and other authors. As is to be seen in the thermogram, talc loses its OH group but at ca. 950°C. There is no other characteristic peak in the curve of talc.

Pyrophyllite. In case of pyrophyllite, the d. t. a. curves given by various authors are not perfectly concordant. That is probably to be ascribed, besides the differences in sensitivity of the instruments, chiefly to the uncertain determination of the samples investigated. E. g. F. H. NORTON [127] observed at 625° C, such a plain endothermal peak, that makes the detection of pyrophyllite by d. t. a. rather uncertain, according to this author. W. F. BRADLEY and R. E. GRIM [7] have found a definite endothermal peak in the curve of the pyrophyllite sample they investigated, but no other peak appeared in their curve (curve No. 4 in plate XII). However, on the basis of d. t. a. curves drawn by P. F. KERR, I. L. KULP, and P. K. HAMILTON it seems that the endothermal peak which ends at 800° C and which is connection with the escape of OH, is followed at ca. 1000° C by an exothermal peak representing the formation of γ aluminium oxide. The latter is to be seen in curves Nos. 5 and 6 of plate XII. Both curves show at 575° C a quartz peak too. The quartz was presented in the sample as an impurity.

Montmorillonoid minerals which should be treated in this group too, will be classed into a separate group among the clay minerals.

Micas. Muscovite. D. t. a. curves published by various authors are not concordant either in the case of muscovite. According to R. E. GRIM and R. A.

ROWLAND [62], the muscovite curve shows a large endothermal peak between 750 and 950° C and unimportant small peaks at 300 and 400° C, respectively. The latter peaks are probably due to adventitious impurity, for e. g. in the curves published by I. BARSHAD they do not appear at all.

After the two muscovite thermograms to be seen in plate XIII, we present the curve of paragonite, closely affined to muscovite, which is also in accordance to BARSHAD. The curve is similar to the former ones, the large plain peak, however, takes place somewhat sooner in the latter case.

As for thermal analysis of glauconite, there are many and mostly concordant data in the literature referring hereto. M. SABATIER has investigated three glauconite samples of various ages and localities, their thermograms were similar to each other. The d. t. a. curve of glauconite unfortunately resembles very much those of illite and other hydromica-like minerals, for this reason its determination requires the utmost care and circumspection. The curves show three endothermal peaks, the first appears at about 150 to 200° C, the second, smaller one at ca. 600° C, the third, the smallest peak over 900° C. According to available data published by various authors, the difference between the curves of glauconite and illite probably consists, in the fact that the third endothermal peak of illite is immediately followed by an exothermal peak, which does not appear in glauconite curves (or at least, if it appears, less distinctly). The d. t. a. curve of seladonite is very similar to that of glauconite, and its determination or rather its distinction from glauconite, is impossible on this basis.

f) *Chlorite group*

The papers by M. J. ORCEL [130], N. S. KURNAKOV and V. V. CHERNYCH [101] on d. t. a. of chlorites were published at about the same time. D. t. a. curves of the most various kinds of chlorite investigated by these authors, have not been perfectly concordant, nevertheless in most cases there appear two endothermal peaks (of dehydration), the first one at ca. 650° C, the second at about 850° C (curves 1 and 2 in plate XIV) but these peaks appear in many cases at a lower temperature, at other times the second peak almost completely disappears, lastly in some cases exothermal peaks appear too, the latter ones are probably due to oxidation processes (curves 3, 4, 5 and 6 in plate XIV). The chlorite curve published by GRIM and ROWLAND [62] is of a quite different character (see curve 7). G. SABATIER [146] has carried out interesting experiments, in order to explain the above-mentioned differences. He started from the supposition, that in case of as large-sized crystals as those of chlorite, the particle size without doubt plays a more important part in the development of the thermogram, than in case of fine-grained substances (e.g. clays). He presents d. t. a. curves of four chlorite samples, first investigated in the coarse-

grained state, in the second place we see the thermograms of the same samples after previous powdering. The investigations of SABATIER are shown in plate XV. This author sums up the results of the investigation as follows: 1. There is a great difference between the thermograms of coarse-grained chlorites. That is in perfect accordance with former observations, e.g. with those of ORCEL. 2. There is a great difference between d. t. a. curves of chlorite, if the same sample is investigated, first in coarse-grained state and then powdered. In the case of the first two samples the peaks are shifted towards lower temperatures, the second sample shows a greatly widened peak, on the other hand samples 3 and 4 distinctly show only one peak instead of two, while in case of powdered samples the exothermal peaks — which are hardly observable originally — become stronger. The third conclusion of the author is probably the most important one in respect to d. t. a.: he points out, that thermograms of fine-powdered samples are of the same type. Consequently there is a possible hope, that the contradictions observed in the course of the thermal analysis of chlorites will be eliminated, and the method will be unequivocally applied to the detection of chlorites.

g) *Vermiculites*

I. BARSHAD [5] has studied in detail the particularities of vermiculites and he pointed out, that one of the most remarkable peculiarities of these minerals consisted in reversible cation-exchangeability, which surpassed even that of montmorillonites. In natural vermiculite the exchangeable cation is Mg, or perhaps Ca. These experiments are very important in respect to d. t. a., because they facilitate the interpretation of d. t. a. curves. In the thermogram of natural vermiculite the following peaks are to be seen: between 100 and 120° C a very small endothermal peak representing the escape of water, absorbed on the surface. This is soon followed by a large endothermal peak marking the escape of non-constitutional water, absorbed between the layers. The maximum of this peak takes place somewhat under 200° C. Thereafter we can observe a third, even smaller, endothermal peak between 250 and 300° C, marking, like in the case of montmorillonite, the escape of the water bound to the exchangeable cation. A further endothermal peak follows at ca. 800° C. This one represents the escape of constitutional OH radicals, at the same time the structure is destructed, and an enstatite structure is formed at the exothermal peak immediately following on the endothermal peak.

On the basis of the investigations by BARSHAD, one may point out how much the peaks resulting from the escape of adsorbed water are affected by the quality of the exchangeable cation. E.g. the small endothermal peak at 280° C only appears in case of Mg and Ca cations, in vermiculite saturated with Na the small peak does not take place (an analogy with montmorillonites!), in case

of vermiculites saturated with K and NH_4 all peaks representing adsorbed water disappear, as a proof that the exchangeable cation considerably affects the amount of water absorbed between the layers. In plate XVI d. t. a. curves of vermiculite are shown, first in the natural state, and after previous saturation with various cations respectively.

h) *Feldspars*

Concerning d. t. a. of feldspars, there is but one reference, namely a paper by A. KÖHLER and P. WIEDEN [91] published in 1954, showing d. t. a. curves of five feldspar samples.

All five of the thermograms distinctly show an endothermal peak appearing between 700 and 900° C. It is particularly distinct in the case of albite (curve 1 in plate XVII) and of one of the anorthites (curve 4). The most likely is that the endothermal peak represents an inversion from the low temperature modification into the high temperature modification. This observation is supported by the fact, that curve 5 of the figure, recorded from a Japanese anorthite sample, does not show any sharp endothermal peak, however, it has been demonstrated by an optical investigation of the same sample that it originally occurred as a high-temperature modification.

KÖHLER and WIEDEN have only investigated the plagioclases, but they pointed out, that the investigation of orthoclases might be much more interesting, for, as far as can be foreseen, d. t. a. curves of the latter would not only show the formation of the high-temperature modification, but also the remixture of perthites. Furthermore, they would regard the investigation of potash feldspars as important, for if one ever succeeded in tracing, by means of d. t. a., in a simple way, whether the potash feldspar present represents the low-temperature modification or the high one, an important datum would be furnished thereby on granitization. They intend to continue their investigations in this matter.

5. Clay minerals

As it has been mentioned above, the group of clay minerals is one of the most important and, at the same time the most thoroughly studied groups, in respect to d. t. a. Since microscopical determination of these minerals encounters certain difficulties because of their fine particle size, the investigators of this terrain are particularly in need of d. t. a. investigations, besides X-ray investigations, and it is due to this fact, that we have the greatest number of data — which are at the same time the most reliable ones — on this very group.

Literature concerning d. t. a. of clay minerals, has recently been enriched by two important monographies. One is a paper entitled "The Differential

Thermal Investigation of Clays" by R. C. MACKENZIE, published in 1957 in an edition of the Mineralogical Society of London, unfortunately it is unaccessible for us. The other monographic work is a description of the clay minerals of Czechoslovakia by J. KONTA [90] containing a great number of d. t. a. curves.

We shall treat clay minerals in the usual way, by dividing them into three main groups, to begin with the minerals of the kaolin group, then follow the montmorillonoid minerals, finally the illite-like minerals.

a) *Minerals of the kaolin group*

Kaolinite, the most important member of this group, is perhaps the most thoroughly investigated mineral in respect to its thermal behaviour. The thermogram of this mineral, shows between 570 and 600° C, a strong endothermal peak which is symmetrical in respect to the bisector drawn from the normal peak to the base line. At this peak, the kaolinite loses the constitutional OH radicals, its crystal structure breaks down. Another peak appears in the thermogram between 950 and 1000° C, this is a sharp exothermal peak, representing the inversion of the amorphous aluminium oxide into γ aluminium oxide. In minerals of other types, this recrystallization process of aluminium oxide takes place sooner, e. g. the exothermal peak, marking the same process in alunite takes place much sooner, but in case of minerals belonging to the kaolin group the SiO_2 content retards the process of crystallization. However, the exothermal peak is not in every case equally sharp, but this depends on the degree of crystallization. On the other hand, the sharpness of the endothermal peak depends on the particle distribution as it has been pointed out, in general in connection with the theoretical considerations treated in part I.

In certain cases, the shape of the d. t. a. curve of kaolinite may be affected by the impurities. R. M. GRUVER, E. C. HENRY, and H. HEYSTEK [68] investigated the effect of iron oxide on the thermogram of kaolinite, and they pointed out, that iron oxide did not cause any considerable change. However, if kaolinite is mixed with certain impurities, the melting point of which is lower than the temperature of the exothermal peak of kaolinite, the peaks, and particularly the exothermal peak, will be smaller. In plate XVII we expose after some kaolinite curves, the change of the exothermal peak of kaolinite upon the effect of Na_2CO_3 and NaCl , on the basis of the above mentioned authors' experiments.

The thermal curve of nacrite is very similar to that of kaolinite, there is but one difference, namely the endothermal peak appears at ca. 60 to 70°C, higher than that in case of kaolinite, as a proof that the lattice of nacrite is somewhat more stable. The peak is much plainer and broader than that of kaolinite, there often appears a double peak, which is probably due to dickite, present as an impurity. According to our experience, the exothermal peak also

appears at a somewhat higher temperature than that of kaolinite, in this case, however, the difference is insignificant.

In the d. t. a. curve of *dickite*, the endothermal peak appears at a still higher temperature, at ca. 700° C. It occurs most frequently in nature together with nacrite, but the occurrences of these minerals are in general relatively scarce. In plate XIX after some thermograms of nacrite and dickite, Hungarian occurrences of both minerals are shown too.

The d. t. a. curve of *halloysite* is likewise very similar to that of kaolinite, nevertheless they are well distinguishable from each other. Namely halloysite has an endothermal peak between 100 and 200°C too, resulting from the loss of adsorbed water. A further difference consists of the fact, that the endothermal peak of about 600° C of halloysite appears at a somewhat lower temperature (560 to 570° C) than that of kaolinite, the shape of the peak is usually asymmetrical, but the ascendant side is generally steeper than the descendant one. As for the theories concerning the structure of halloysite, the thermogram of halloysite is mostly in accordance with that of HENDRICKS; according to this theory the halloysite contains certain layers, the composition whereof is identical to that of kaolinite, and the water-content of halloysite takes place between these layers as molecular water. The halloysite which has lost its molecular water is called metahalloysite. The halloysite-metahalloysite alteration is an irreversible process.

"Fireclay" also belongs to the kaolin group, on the basis of its d. t. a. curve, as it represents a transition between kaolinite and halloysite. The endothermal peak appearing in case of halloysite (over 100° C) is less intensive than in "fireclay" minerals, otherwise the curve is similar to that of kaolinite. In recent investigations it has been pointed out, that the structure of this mineral was a transitional one too, and it seems that these minerals represent a sort of continuous transition between kaolinite and halloysite. GRIMSHAW, HEATEN and ROBERTS have drawn up a very instructive table on the peaks of thermal curves of kaolinite, halloysite, and "fireclay", this table clearly shows the above-mentioned transitional character [63].

Mineral	Temperature of the first endothermal peak	Temperature of the main endothermal peak	Temperature of the exothermal peak
Kaolinite	—	583 ± 3° C	980° C
Halloysite	143 to 148 ± 3° C	547 to 555° C	965 to 972° C
"Fireclay" minerals	138 to 150 ± 3° C	550 to 562° C	940 to 950° C

In the course of d. t. a. investigations carried out at the Hungarian State Geological Institute the whole kaolinite-"fireclay"-halloysite series appeared in a very interesting way, in samples which came to hand from the kaolin prospecting at Szegilong (see plate XX).

BELYANKIN has found a sort of kaolin, in the thermogram of which the endothermal peak is absolutely identical to that of kaolin, but the exothermal process between 950 and 1000° C is completely missing. This mineral has been called monothermite by Soviet investigators, on the initiative of BELYANKIN. The monothermite is considered as a kaolinite mineral of mixed structure, but by experiences obtained from the thermogram of kaolinite, it can be supposed, that monothermite is in fact a badly crystallized kaolin where the exothermal peak is missing in consequence of the low degree of crystallization.

b) *Montmorillonoide minerals*

Thermograms of various minerals of the montmorillonoide group show many identical characteristics. First of all, each one has an endothermal peak between 100 and 250° C, resulting from the escape of adsorbed water. The following, likewise an endothermal peak takes place between 500 and 800° C, the respective temperatures sufficiently characterize each member of the group. The latter peak marks a partial escape of OH radicals of the lattice. Finally, a third endothermal peak at ca. 900° C represents the escape of all constitutional OH radicals and a total breaking down of the lattice. In most cases, this peak is immediately followed by an exothermal peak, attributed to the formation of spinel which takes place directly after the destruction of the lattice. Less important, but characteristic differences between several members of the group will be below treated, in connection with the description of their respective thermograms.

The thermal curve of montmorillonite was examined by many investigators. Concerning the first endothermal peak, the maximum whereof usually takes place somewhat under 200° C, many interesting data have been given by the thorough investigations by S. B. HENDRICKS and his collaborators [71]. They have pointed out, that the escape of adsorbed water was a reversible process. The amount of adsorbed water depends on the relative moisture and on the quality of exchangeable cations. Therefore, the shape or the magnitude of the first peak cannot characterize the clay mineral in question. It has been pointed out in the general part of this paper, too, that for the very reasons mentioned above, no quantitative determination of montmorillonite could be carried out on the basis of the first endothermal peak. The shape of the curve is affected, according to experience, by the quality of the exchangeable cation, or rather by its hydration energy. Plate XXI shows, according to the investigations of I. BARSHAD, the change in the shape of the first endothermal peak, related to the substituted cation. As is to be seen, in case of Ca, Mg, Ba ions, the first peak is double or even treble, on the other hand the peak is simple and the peak area smaller in the case of Na, NH₄, K ions. In the

case of montmorillonite saturated with NH_4 , the exothermal peaks appearing at about 400°C — which do not appear in any other samples — are probably in connection with the escape of NH_3 . In fact the first peak consists of three parts: the peak appearing at 130°C results from the escape of adsorbed water, the second one at 165°C from that of interlamellar water, the third at 220°C from that of the hydrate core of the exchangeable cation.

On the basis of all these, it is obvious to infer on the quality of the exchangeable cation from the shape of the first peak. Hungarian bentonites contain Ca-montmorillonite for the most part, in contrast to Na-montmorillonites which are more frequent in America.

We also have our own experiences on the change of the peaks of Ca- and Na-montmorillonite. Some experiments were carried out by our collaborators in the Hungarian State Geological Institute in order to win montmorillonite in the shape of Na-montmorillonite from bentonites by applying a process of colloid chemistry, in accordance with the method described by BUZÁGH and SZEPESI [19]. We have ascertained that they had sufficiently succeeded in separating montmorillonite from the other minerals and the so won product in every case gave the theoretical montmorillonite curve. In plate XXII, we present, following some American montmorillonite curves, thermograms of Hungarian bentonite occurrences, finally the Na-montmorillonite won from the bentonite of Istenmezeje.

In the thermal curve of montmorillonite, the second endothermal peak usually appears between 670 and 710°C . This peak already marks the escape of the OH radical of the lattice. This is naturally an irreversible process. It is not quite clear, whether all OH radicals escape in the course of this process, or only a part thereof. According to some investigators, there is no more loss of constitutional water at the peak appearing at 900°C , this peak only marking the destruction of the lattice; according to other investigators the OH radicals remaining at 700°C totally escape at 900°C . According to another supposition, one peak represents the OH radicals escaping from the octahedral structure, the other one marking those escaping from the tetrahedral structure. In any case, it may be pointed out, that the substitutions taking place in the lattice, remarkably affect the temperature of the peak appearing at ca. 700°C . In general, the Al-hydroxyl-bond seems to be much stronger than the Fe-hydroxyl-bond, on the other hand the Mg-hydroxyl-bond is even stronger than the Al-hydroxyl-bond. Consequently, in case of those montmorillonite minerals in which Al is substituted by Fe (nontronite, beidellite), the second endothermal peak appears at 100 to 200°C lower than in pure montmorillonite, on the other hand in case of Mg substitutions (saponite, hectorite) this peak appears at about 100°C higher.

The third endothermal peak is also affected by the substitution taking place in the lattice; as the lattice is totally destroyed here, one can observe

the effect of the substitutions taking place in the octahedral structure as much as on those of the tetrahedral structure. The variety of peak temperatures is not perhaps so considerable at this peak as in the former, but one can often observe that the magnitude of the peak decreases without any reason; in many cases we have even seen that the third peak was hardly observable.

The exothermal peak following upon the third endothermal peak is affected anew by substitutions, namely by those of the octahedral layer. In case of Al-Mg-substitution the exothermal peak is sharpened, while it may completely disappear upon the effect of Al-Fe-substitution.

On the basis of all the above described, d. t. a. curves of other members of the montmorillonite group are easily interpreted.

In the thermogram of *nontronite*, after the usual initial large peak of adsorption, the second endothermal peak already appears between 400 and 500° C (high Fe substitution), the third endothermal peak appears at ca. 900° C in this case as well, but it is not sufficiently characteristic and the exothermal peak following thereupon is diminished because of the high iron content. In plate XXIII, we present, after some montmorillonite curves, the thermogram of the nontronite of Užgorod (Ungvár) which has for some time been wrongly called chloropal.

Beidellite has also been formed from montmorillonite structure by Al-Fe substitution. However, while in the case of nontronite the substitution has totally been accomplished, the substitution in beidellite took place only in half. In the d. t. a. curve of beidellite, the second endothermal peak appears — in accordance with our theoretical considerations — somewhat lower than the 700° C peak of montmorillonite, but higher than the nontronite peak taking place under 500° C, i.e. between 550 and 600° C. R. GRIM and A. ROWLAND — though they do not doubt the existence of beidellite as an independent mineral — have pointed out, after having made thermograms of many so-called beidellite samples, that even one of the samples coming from its original locality (Beidell), was a mixture of minerals consisting of halloysite, illite and montmorillonite. Similar observations were made in case of five other so-called beidellite samples by GRIM and ROWLAND. As a matter of fact, it is difficult to decide this question, only on the basis of thermal curves.

Saponite. Its structure is formed by Al-Mg substitution in the octahedral structure. The second endothermal peak appears at about 800° C. CH. KIEFER has interpreted the thermogram of the saponite sample he investigated, as follows: at the first peak of dehydration (with a peak maximum of ca. 180° C), the mineral loses about 23,8% of its water content. The second dehydration results in an endothermal peak between 820 and 860° C. In the course of the latter process the loss of water amounts to 4,6%, corresponding to its constitutional water. Curve 6 in plate XXIII shows a saponite sample investigated by KIEFER; at about 650° C there appears a further endothermal peak,

besides the above-mentioned ones. According to the interpretation of KIEFER the third peak is due to α antigorite. The exothermal peak of antigorite is overlapped by the endothermal peak of saponite appearing over 800° C.

Hectorite usually contains Li, besides Mg. Its thermal curve is similar to that of saponite (curve 7, in plate XXIII).

Sauconite is a zinciferous montmorillonoid mineral. Its thermal behaviour is described by C. S. ROSS [139]. Up to 600° C, sauconite behaves in general, in the same way as montmorillonoid minerals, but over 600° C the formation of new zinc silicates is accompanied by exothermal peaks.

c) *Hydromicas*

Illite. Although illite very frequently occurs in nature, it is very difficult to acquire pure illite in order to determine its thermogram, for in most illite samples, either other sorts of clay minerals occur (e. g. kaolinite) together with illite, or it forms a mixed lattice with montmorillonoid minerals.

The d. t. a. curve of illite is less characteristic than that of montmorillonite. The character of the curve is very similar to that of the montmorillonoid minerals, but the peaks are less distinct, smaller and less sharp. The first endothermal peak, likewise resulting from the escape of adsorbed water, appears between 100 and 200° C, but it is much smaller than in the case of montmorillonite. The second endothermal peak representing the escape of constitutional water appears between 500 and 650° C. Finally, at ca. 900° C, a third, small endothermal peak accompanies the destruction of the lattice. In most cases, the third peak — similarly to that of montmorillonites — is immediately followed by a sharp exothermal peak which may be interpreted by the formation of spinel as well, and which indicates the contamination of illite by montmorillonite. According to R. E. GRIM and W. F. BRADLEY [60] both the first and the second endothermal peaks are reversible, for if the illite sample is heated up to 800° C and then left to stand for a long time, it may recover the water which had escaped from its structure. After the final destruction taking place over 800° C, it is not possible any longer to reconstruct the original structure. The exothermal peak of illite and, in a lower degree, its endothermal peaks are in many cases also irregular. This fact indicates that the structure of illite is neither regular nor uniform; as a matter of fact it represents a mineral group rather than an individual mineral.

As has been pointed out above, it often happens that illite and montmorillonite are interlaced. E.g. the clay called illite of Sárospatak according to literature, (it comes in fact from Füzérradvány) consists, according to the investigations of BRADLEY, of facets, the core of which is illite, altered on the surface into montmorillonite. It follows that the chemical analysis and X-ray

diagram of this mineral correspond to those of illite, but its cation exchange and, in general, the colloidal superficial properties remind one of those of montmorillonite.

In the d. t. a. curves, the mixed lattice is usually recognizable. E.g. in curve 7 of plate XXIV/a one may see both the endothermal peak of illite at ca. 600° C and that of montmorillonite at ca. 700° C. The first endothermal peak resulting from the escape of adsorbed water is larger than is usual in case of illite, but smaller than that of montmorillonites.

We can give some data on Hungarian occurrences of illite proving their general spreading in nature. We investigated Pleistocene clay samples from various localities of the Great Hungarian Plain, and we have pointed out, that the dominant clay mineral of these formations was always illite. (See curves 3 and 4 in plate XXIV/a) Similar data have been obtained by WIKLANDER [174] on Swedish and by SOVERI [157] on Finnish Quaternary clays.

We have to mention in the group of hydromicas, the hydromuscovite of Nagyörzsöny, described by J. ERDÉLYI [35] Curve 1 of plate XXIV/b shows the thermogram taken from this mineral comparing it with the paragonite sample of BARSHAD [5] mentioned in another passage, the curve of which is shown below the former. According to ERDÉLYI, it corresponds in all likelihood to hydromuscovite. This is also supported by the similarity of both thermograms.

Curve 3 of the plate has been recorded from a leverrierite sample published by KONTA.

According to ERDÉLYI, the leverrierite mentioned as hydromuscovite by KONTA, is rather to be qualified as sericite, as its thermogram is also different from the curve of the hydromuscovite from Nagyörzsöny.

d) *Mixtures of clay minerals*

Since it often happens in nature that various clay minerals occur beside each other (mixed or intergrown), many investigators have also studied the thermal curves of mixtures of clay minerals.

R. E. GRIM [58] prepared artificial mixtures of some clay minerals in various proportions. In the case of mixtures of kaolinite and illite (plate XXV) it can be observed, that the detection of these two clay minerals beside each other, on the sole basis of the thermogram, may give rise to some confusion. Possibly the initial peak of illite is misleading, for one might infer the presence of "fireclay" from this peak. The second peak of illite and the large endothermal peak of kaolinite are overlapping. Though the third peak of illite and the small exothermal peak following thereupon are separated from the large exothermal

peak of kaolinite in these curves, these very peaks are not always distinct enough in illite.

The determination beside each other of Ca-montmorillonite and kaolinite is an easier task, because the characteristic peaks of both minerals distinctly appear. Mixtures beside each other of Na-montmorillonite and kaolinite represent an analogous case (plate XXVI).

The determination again becomes more difficult when illite occurs beside montmorillonite, though, as it is to be seen in plate XXVI, the illite peak at about 600° C, and the montmorillonite peak at about 700° C make the presence of both minerals beside each other quite evident.

The two last curves of plate XXVI according to GRIM show the simultaneous presence of kaolinite, illite, and montmorillonite. In this case, the detection of illite is practically impossible, for the first peak is overlapped by that of montmorillonite, the second one by that of kaolinite. Certain anomalies of the curve, however, call attention to the possibility of the presence of this mineral.

e) *Special clay minerals*

On plate XXVII d. t. a. curves of two *allophanes* are presented, according to W. A. WHITE [170]. Curves 1 and 2 were taken after previous desiccation of the sample at 110° C — during one night — curves 3 and 4 are thermograms of the same samples in their original state of moisture. As it can be observed, the originally absorbed moisture of the allophane samples is rather high. The small endothermal peak appearing over 500° C is probably due to a contamination by some other mineral. The exothermal peak over 1000° C marks the formation of a new modification. Allophanes are not crystalline, but amorphous clay minerals, however because of the exothermal peak which is observable at about 1000° C in their thermogram, they are usually treated among the kaolin group of minerals.

The last curve of plate XXVII was taken from *dillnite*, a special clay mineral. This mineral occurs in the region of Banská Belá, Czechoslovakia, and was described more than a 100 years ago by HUTZLEMANN. This mineral up till now was considered as a mixture consisting for the most part of kaolinite and diaspore. J. KONTA [89 and 90] has recently pointed out that dillnite was a special clay mineral with high Al_2O_3 content. The thermogram of this mineral according to KONTA is shown in plate XXVII. The curve shows that there is practically no loss of adsorbed water. This mineral loses its constitutional water at an unusually high temperature, between 700 and 900° C, the maximum of its endothermal peak being at ca. 860° C. Only talc and muscovite are dehydrated at such high temperatures, but the peaks of these minerals are much plainer. The thermogram of pyrophyllite is also of a quite different type. Consequently.

on the basis of the d. t. a. curve, KONTA has been able to point out, that dillnite was a clay mineral of high hygroscopicity and, on the other hand, the OH groups were very strongly bound in the crystal lattice,

In addition we mention that we ourselves carried out a d. t. a. test of the dillnite sample of the Hungarian National Museum, after the publication of KONTA's paper and the results we obtained were in accordance with his. We can complete his results with the fact, that we continued this investigation up to 1150° C in order to determine whether a second peak would appear over 1000° C. It has been proved that no further peak appeared in the thermogram up to the above-mentioned temperature.

6. Phosphates

In the course of the thermal analysis of phosphates, processes involving heat change take place at dehydration, dissociation, and inversion from one modification into another. Consequently, it is quite probable, that some characteristic peaks appear in the thermogram of most phosphate minerals.

R. J. MANLY [117] has determined d. t. a. curves of 14 phosphate minerals and interpreted the peaks appearing in the curve (plate XXVIII). Most phosphate minerals (variscite, bolivarite, lazulite, wavellite, evansite, bobierrite, vivianite, zepharovichite [?]), show an endothermal peak, each at low temperatures between 100 and 300° C, marking the escape of crystal water. In many cases, a second endothermal peak appears at a several hundred degrees higher temperature, this one usually marks the escape of constitutional OH. Exothermal peaks appearing at higher temperatures represent recrystallization. Curve 7 taken from an artificial berlinite mineral (AlPO_4) is particularly remarkable. This curve is very similar to that of quartz, but in this case the peak appears at 585° C, i.e. 10° higher than the quartz peak. This peak represents an inversion, namely the α modification $\rightarrow \beta$ modification inversion.

The extraordinarily twisted peaks of MANLY's phosphate thermograms are obviously to be attributed to the recording equipment used by this author. The figures show that the pen arm of the recorder did not record straight, but along a circular arc.

One can find only one reference concerning fluorapatite: according to S. R. SILVERMAN, R. K. FUYAT, and J. D. WEISER [155], the thermal curve of fluorapatite does not show any bending up to 950° C.

In 1957, a new aluminium phosphate was described under the name of kingite ($\text{Al}_2\text{O}_3 \cdot \text{Al}(\text{OH})_3\text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$) by NORRISH and his collaborators [126]. We present the curve of this mineral in plate XXVIII/b.

7. Sulfates

In the d. t. a. curves of anhydrous sulfates, peaks generally appear in consequence of polymorphous alterations or possibly from fusion. In case of hydrous sulfates, dehydration may naturally result in endothermal peaks. Besides, some other processes, e.g. oxidation, change in valence, decomposition etc., can take place in certain sulfate minerals.

We have a small number of references on d. t. a. of sulfates at our disposal, except for gypsum and alunite. A long-needed work has been carried out in this terrain by A. J. CVETKOV and E. P. VALYASHINA [26]. Their paper of more than 100 pages gives an overall view of the thermal behaviour of sulfates.

In the thermal curve of thenardite (Na_2SO_4) one may observe two endothermal processes (see plate XXIX). The first process starts at 230°C , reaches its maximum at 270°C , this is a reversible polymorphous alteration. The second endothermal process takes place at 890°C , it marks the fusion of thenardite.

The thermogram of glauberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$) similarly shows two endothermal peaks. The first peak starts at 520°C , reaches its maximum at 540°C , this peak represents the decomposition of double salt into CaSO_4 and Na_2SO_4 . At the second peak (890 to 910°C) the substance fuses.

The thermal curve of baryte does not show any peak in the course of heating up to the usual degree (1000°C), but at 1150°C there appears an endothermal peak resulting from a polymorphous alteration of the baryte. This peak is reversible, it appears in the cooling curve, on the same temperature as that of the exothermal peak (curve 3 in plate XXIX).

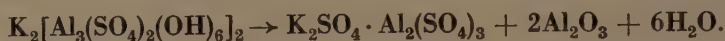
The thermogram of anglesite (PbSO_4) shows an endothermal peak at 860°C in consequence of a polymorphous alteration, in addition, according to CVETKOV and his collaborator, there appears a second endothermal peak at 960°C , after repeated heating and cooling. They, however, were not able to give a reason for the latter peak.

The thermal curve of anhydrite (CaSO_4), similarly to that of baryte, does not show any process involving change in heat content up to 1000°C , but from 1190°C on, an endothermal peak with a maximum of 1200°C appears in the anhydrite sample heated over 1000°C . This peak results from a polymorphous alteration, too (curve 5 in plate XXIX). Since the thermogram of gypsum is different from that of anhydrite because of dehydration, d. t. a. can be employed as an easy method in geological research, for the purpose of distinguishing gypsum from anhydrite.

The thermal curve of coelestine (SrSO_4) is very similar to that of baryte; at about the same temperature, from 1145°C on, it shows an endothermal curve which is due likewise to a polymorphous alteration. This process is also reversible (curve 6 in plate XXIX).

The thermal behaviour of the members of alunite and jarosite series were thoroughly examined by J. L. KULP and A. H. ADLER, besides the above mentioned authors. There is no considerable difference of opinion between the respective authors.

In the d. t. a. curve of alunite (see curves 1 and 2 in plate XXX) one can see two large endothermal peaks and a small endothermal one. The maximum of the first large endothermal peak takes place at ca. 550° C. At this peak the lattice of alunite is destructed during dehydration. The process of decomposition is the following :

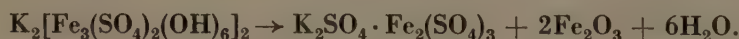


Over 760° C, the recrystallization of α Al_2O_3 begins at a small exothermal peak which, however, shortly turns into a large endothermal peak, marking another decomposition as follows :



According to certain authors, the maximum of the second peak takes place between 810 and 850° C.

In consequence of the structural analogy, the curve of *jarosite* is very similar to that of alunite, the only difference between both these thermograms consists in the values of the peak temperature. In case of jarosite, the first endothermal peak appears at an about 100° C lower temperature, i.e. at ca. 460° C, as a proof that the Fe-OH bond is looser than the Al-OH bond. The process of decomposition is similar to that of alunite :



Fe_2O_3 produced in this way is recrystallized as soon as the process of decomposition is ended, while the recrystallization of Al_2O_3 formed in the course of decomposition of alunite takes place at a higher temperature. The recrystallization of hematite is marked by a small exothermal peak immediately following on the first endothermal peak. The second endothermal peak of jarosite starts at 700° C, this dissociation takes place according to the following equation :



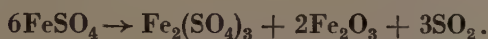
The temperature of this decomposition is also somewhat lower than in the case of alunite.

In plate XXX according to KULP and his collaborators, we also show d. t. a. curves of plumbojarosite and argentojarosite.

The thermograms of hydrous sulfates show endothermal peaks in consequence of dehydration. The position and shape of these peaks are, however, characteristic of the respective minerals (plate XXXI.).

In the thermal curve of *gypsum* ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) one may observe between 100 and 200° C a large endothermal peak, one molecule and a half of water escapes at the first endothermal peak, the residual half escaping at the second peak. Thereafter the curve completely corresponds to that of anhydrite, since a further endothermal peak appears only over 1180° C in consequence of polymorphous alteration of anhydrite.

The dehydration of *melanterite* ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) takes place in three steps, between 60 and 320° C. In addition, the thermogram of melanterite is complicated by many more or less large endothermal and exothermal peaks. According to the explanation given by CVETKOV and his collaborator, the processes taking place between 425 and 550° C mark the alteration of ferrous sulfate into ferric sulfate which may be expressed by the following equation :



In the course of the last endothermal process, between 650 and 750° C, the ferric sulfate is totally dissociated into Fe_2O_3 and SO_3 .

In the thermal curve of *epsomite* ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) one may observe, between 50 and 350° C, seven endothermal peaks, all of them resulting from gradual dehydration. Meanwhile various intermediate hydrates are formed. There is no peak between 350 and 1000° C, but a further endothermal process takes place over 1000° C. The latter process is reversible being in connection with a polymorphous alteration of MgSO_4 .

The d. t. a. curve of *mirabilite* ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) shows four endothermal processes ; the first one appears between 30 and 40° C, when the false fusion of sodium sulfate takes place. At 100° C the water evaporates, the residue of this process is anhydrous sodium sulfate. The third peak appearing between 230 and 240° C, is known from the curve of thenardite, it is the result of the reversible polymorphous alteration of thenardite. The fourth peak appearing between 884 and 910° C marks the fusion of Na_2SO_4 .

The dehydration of *chalcantite* ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) takes place in three steps. Two molecules of water escape at each of the first two endothermal peaks (between 85 and 95° C, 110 and 120° C respectively), while at the third endothermal peak (between 240 and 320° C) the residual monohydrate loses the last molecule of water. The thermal curve shows, besides the peaks marking dehydration, two further endothermal peaks over 800° C. The processes are irreversible, they result from the dissociation of cupric sulfate, which takes place in two steps.

In the thermal curve of *aluminite* ($\text{Al}_2(\text{SO}_4)(\text{OH})_4 \cdot 7\text{H}_2\text{O}$) a double endothermal peak marks gradual dehydration between 100 and 250° C. At ca.

840° C a sharp exothermal peak represents the dissociation of aluminite (according to the interpretation of CVETKOV and his collaborator) into Al_2O_3 and $\text{Al}_2(\text{SO}_4)_3$.

The latter still dissociates at about 890° C into Al_2O_3 and SO_3 . An aluminite curve very similar to that of CVETKOV is published by T. GEDEON in a description of the aluminite of Gánt [50].

8. Carbonates

D. t. a. has an important role in the investigation of carbonates, for, on the one hand it furnishes informations on the mechanism of decomposition of carbonates, on the other hand it gives data which facilitate a rapid determination of these minerals. Consequently there are a great number of references concerning the d. t. a. of carbonates.

In the thermal curve of *calcite*, one single large endothermal peak appears between 800 and 900° C, marking the dissociation of it. J. L. KULP, P. KENT and P. F. KERR [94] have examined how far particle sizes were affecting the temperature of the peak marking dissociation, and they pointed out, that particle sizes affected both the initial temperature of the endothermal peak and that of the peak maximum. Peak temperatures varied, according to the above-mentioned authors from 880° C to 930° C, in proportion to the particle sizes.

It is problematical, whether the thermogram of aragonite is identical to that of calcite. It has been proved by the investigations of G. T. FAUST [38], that besides the great endothermal process taking place over 800° C, a further, small endothermal peak, varying between 387 and 488° C, appeared in the thermal curve of aragonite. This small endothermal peak represents the monotropic aragonite \rightarrow calcite alteration, i. e. it does not appear in the cooling curve. After this alteration the curve is naturally identical to that of calcite. As the alteration heat is small, a sufficiently sensitive d. t. a. apparatus is required for reliable observations. However, it follows that calcite and aragonite are discernible by means of suitably sensitive apparatus (plate XXXII).

Concerning the thermal curve of *magnesite*, there are far too many references which only contain insignificant inconsistencies. This is obviously due to the impurity of the samples investigated. The maximum of the great endothermal process marking the dissociation of pure magnesite takes place between 670 and 720° C. According to KULP, KENT and KERR [94], the effect of the particle size on the peak temperature is less important than in the case of calcite. P. WIEDEN [170] points out, that following the endothermal peak of most magnesite samples, there appears a small exothermal peak at ca. 705° C too. According to WIEDEN, this peak represents the heat of crystallization required for the alteration of

magnesium oxide into periclase. Curve 4 of plate XXXIII was taken from a magnesite containing some Fe in its lattice. The presence of iron is indicated by the exothermal peak following on the large endothermal peak; the exothermal peak results from the oxidation of iron. The small endothermal peak appearing over 800°C is due to a contamination by calcite. The calcite peak here appears sooner than e. g. in curve 1, because in case of applying the usual methods for the determination to small amounts, the peak temperature is generally shifted towards lower temperatures (for details see Part I).

The thermal dissociation of *dolomite* ($\text{CaMg}(\text{CO}_3)_2$) takes place in two steps. The first step consists of the dissociation of magnesium carbonate, the second in that of calcium carbonate. Consequently, two sharp endothermal peaks appear in the thermal curve of dolomites; at the first peak, at ca. 800°C , MgCO_3 is dissociated and altered into periclase, at the second one the dissociation of CaCO_3 takes place at about 910°C . It was quite some time ago that G. T. FAUST [36] took note of the fact, that the endothermal peak of magnesite appeared some 130°C lower, than the peak marking the dissociation of magnesium carbonate of the dolomite, the calcite peak, on the other hand, was somewhat higher than that of calcium carbonate of the dolomite. It follows that dolomite and magnesite beside each other are discernible or rather determinable by means of d. t. a. This conclusion of FAUST was also supported in the course of our investigations carried out in the Hungarian State Geological Institute [46]. We prepared from pure CaCO_3 and pure MgCO_3 a series of artificial mixtures containing the above mentioned constituents in the same proportion as they are present in the dolomites investigated in our Laboratory. In every case we found that MgCO_3 of the mixture was dissociated at a far lower temperature than that of dolomite. Curve 6 of plate XXXII was taken from a mixture of CaCO_3 and MgCO_3 corresponding in proportion to the dolomite of Nyirád-Cserhegy, represented in curve 5. As is to be seen, there is a difference of 125°C between the respective first peak temperatures.

In many cases, however, the dissociation of dolomite produces certain irregularities which are also to be taken into consideration in the evaluation of d. t. a. results. L. G. BERG [12] and recently D. L. GRAF [56] called attention to the fact that, on the effect of alkali salts, the first peak of dolomite appeared at lower temperatures.

Concerning the anomalies of thermal dissociation of dolomite, systematic investigations were carried out by M. FÖLDVÁRI-VOGL and V. KOBLENCZ [46] too. They examined the effect of various soluble and insoluble alkali and earth alkali salts on the dissociation of dolomite. They pointed out, that as much as 0,1% NaCl perceptibly decreased the temperature of the first peak of dolomite. This effect shows an upward tendency, if the concentration of NaCl is increased, but it touches its maximum at 5% NaCl. If the degree of contamination by NaCl becomes higher, the peak temperature does not decrease any more.

However, other sorts of alkali salt have considerably more effect. In general, peak temperature decreased mostly on the effect of alkali nitrates. The effect of the soluble salts of alkali earth metals is somewhat lower. Insoluble salts did not affect the temperature of the peaks of dolomite.

For the sake of clarity, we here tabulate the peak temperatures, appearing on the effect of various salts. We have to remark, that the results given in the table, represent in each case the effect of 5% admixed salt impurity. The experiments were carried out on the sample from Nyirád-Cserhegy, presented in plate XXXII.

Salt admixed to dolomite	Temperature of the first peak	Salt admixed to dolomite	Temperature of the first peak
Pure dolomite	780 °C	Pure dolomite	780 °C
+LiCl	520	+K ₂ SO ₄	740
+NaCl	710	+Rb ₂ SO ₄	660
+KCl	695	+MgCl ₂	710
+RbCl	670	+CaCl ₂	700
+CsCl	610	+SrCl ₂	650
+Li ₂ CO ₃	690	+BaCl ₂	700
+Na ₂ CO ₃	620	+MgCO ₃	640 and 780
+K ₂ CO ₃	670	+BaCO ₃	790
+LiNO ₃	500	+Mg(NO ₃) ₂	650
+NaNO ₃	570	+Ca(NO ₃) ₂	600
+KNO ₃	570	+Sr(NO ₃) ₂	540
+RbNO ₃	575	+Ba(NO ₃) ₂	790
+CsNO ₃	575	+MgSO ₄	620
+Li ₂ SO ₄	650	+CaSO ₄	790
+Na ₂ SO ₄	720	+BaSO	790

As for the interpretation of this phenomenon, the author and her collaborators had to be content with suppositions, which as yet are not proved.

Quite recently, we were able to complete these investigations by some new observations. On the one hand we have pointed out that the soluble salts did not affect the dissociation temperature of calcite, but changed the dissociation of magnesite in the same sense as that of the dolomites. Further on we examined the effect of Fe₂O₃ and AgCl on the dissociation of dolomite. Fe₂O₃ did not perceptibly affect the position of the dolomite peaks, while on the effect of 10% AgCl, the temperature of the first peak of dolomite rose by some 30 to 40°, consequently we observed that AgCl rather retarded the dissociation. We intend to continue these investigations.

We have dwelt on all these phenomena because in the course of our investigations until now, we examined dolomites of such an anomalous peak in many cases but for the most part we succeeded in washing out the troubling impurity from the dolomite sample. Thereafter the dolomite peaks appeared regularly, consequently the evaluation of the investigation of the sample became practicable.

Huntite ($\text{Mg}_3\text{Ca}(\text{CO}_3)_2$), a rare mineral, was first described by G. T. FAUST [39]. In the d. t. a. curve of this mineral, endothermal peaks appeared at 644 and 900° C. It is mainly distinguishable from dolomite by the proportion of the respective peak areas. Namely, in the case of dolomite the proportion of the peak marking the dissociation of MgCO_3 to that marking the dissociation of CaCO_3 is about 3 to 5, in case of huntite 4 to 2. A Hungarian occurrence of huntite was described by V. KOBLENCZ and E. NEMECZ [85].

Many authors have dealt with the thermal behaviour of *siderite* [94, 142, 79]. They pointed out, that the dissociation of siderite into ferrous oxide was an endothermal process the temperature of which varied within a very wide range, 500 to 600° C. The reason for this fluctuation is partly ascribed to the differences in particle size, partly to a partial substitution of Fe^{++} ion by Mn^{++} and Mg^{++} ions. In the case of pure, medium-grained siderite, the value of peak temperature is probably about 550° C. Most siderite samples show, immediately after the endothermal peak, a large exothermal peak representing the oxidation of FeO into Fe_2O_3 . In most cases a further smaller exothermal peak appears following the large exothermal peak in the thermograms of siderite samples. According to KULP, KENT, and KERR [94] the latter peak results from the fact, that maghemite is also formed at the first large exothermal peak besides hematite. At the second exothermal peak maghemite (γ ferric oxide) is totally altered into hematite (α ferric oxide).

One may often find a steplike bend on the descending side of the endothermal peak of the thermograms of siderites. We quite frequently observed this phenomenon in the course of our investigations of siderite samples from Rudabánya, too. V. I. KAURKOVSKY [79] had explained this phenomenon by the heterogeneous particle sizes of siderite samples showing the above-mentioned steplike bend. A fine-grained and a coarse-grained structure was, even optically observable, in the microstructure of siderites. The steplike shape of the curve is due to the differences between dissociation temperatures of the two kinds of particle sizes.

Ankerite is substantially a sort of dolomite, wherein Mg is for the most part substituted by ferrous ion. In the thermogram of ankerite one may observe three endothermal peaks. As for the interpretation of the peaks, there are some differences of opinion among various authors. According to KULP, KENT, and KERR [94] the first peak appearing between 650 and 750° C (its respective position depends on particle sizes and degree of iron substitution) marks the

escape of CO_2 bound by the position of Mg. The higher the Fe^{++} content of the carbonate sample, the larger the second peak, appearing at ca. 850°C , consequently, according to the above-mentioned authors, it cannot be brought into connection with the dissociation of MgCO_3 , as has been suggested by BECK [10]. The third endothermal peak as well as that of dolomite represents the dissociation of CaCO_3 . In the case of samples of high iron content, the oxidation of the ferrous ion is shown by an exothermal peak following the first endothermal peak. It may be supposed that the second endothermal peak marks the formation of a compound which can be denoted by the following formula: $\text{Fe}_2\text{O}_3 \cdot \text{CaCO}_3$.

The thermal behaviour of *manganous carbonates* is treated, in detail, in a paper by KULP, WRIGHT, and HOLMES [100]. In the thermal curve of pure rhodochrosite, a sharp endothermal peak appears between 580 and 610°C , marking the dissociation of the carbonate and loss of CO_2 . If the investigation is not carried out in a vacuum, the endothermal peak is immediately followed by an exothermal one (at about 720 to 750°C), too. The latter results from the oxidation of bivalent manganese. If the manganese of rhodochrosite is partially substituted by calcium or magnesium, the substitutive ions increase the bond strength in the carbonate lattice, and the temperature of the endothermal peak marking decomposition rises in proportion to the amount of the respective Ca or Mg ions. Conversely, if the manganese ions of rhodochrosite are partially substituted by ferrous ions, the latter decrease the bond strength, and diminish the peak temperature a little. On summing up, one may point out, that in case of ion substitutions, the dissociation of manganous carbonate containing various sorts of cations is marked in the curve by one single peak, the temperature of which depends on the quality and quantity of the exchangeable ions.

On the other hand, when various carbonate minerals are present beside each other (e. g. mixture of calcite and rhodochrosite etc.), the thermogram separately marks the decomposition of each mineral, at the respective characteristic temperatures. Consequently, one may determine by d. t. a., whether e. g. manganous calcite or a mixture of calcite and rhodochrosite is present. In connection with the investigation of the carbonate manganese ores of Urkut and Eplény — in the Hungarian State Geological Institute — we have also collected a lot of data on the thermal behaviour of carbonate manganese minerals [47]. We met with some methodical difficulties, principally in detecting siderite and rhodochrosite beside each other. Namely, there is not more than 30 to 50°C difference between the peaks marking the dissociation of the respective two carbonates. Consequently the two peaks do not appear separately, but they show a single widened peak. Such an incertitude is eliminable in many cases by our "compensating" method, exposed in Part I (see p. 20).

The formation of the peak of rhodochrosite can also be troubled by the presence of pyrolusite. I. e. the first endothermal peak of pyrolusite falls in

the same terrain of temperature as the exothermal peak of rhodochrosite, thus the two opposite heat effects may hinder the development of both peaks.

In addition, we have to mention that, according to J. KONTA [87], the peak of rhodochrosite considerably decreases in the presence of pyrite and melnikovite.

In plate XXXIV, we present d. t. a. curves of some other carbonates, according to R. M. GRUVER [67].

Strontianite (SrCO_3) does not dissociate up to 1250°C , it shows however an endothermal process at about 930°C , resulting from an inversion of the rhombic modification into the trigonal one.

The dissociation of *witherite* (BaCO_3) takes place at a still higher temperature, but in consequence of an inversion from one modification into another it produces some endothermal peaks even up to 1000°C ; by means of these peaks the determination of the mineral is feasible, even if the investigation is interrupted at the above-mentioned temperature. In the d. t. a. curve of *witherite* one may observe two endothermal peaks, the first one marking the α modification $\rightarrow \beta$ modification inversion at about 820°C , the second one marking the β modification $\rightarrow \gamma$ modification inversion at about 975°C .

The dissociation of *cerussite* (PbCO_3) results in two endothermal peaks at 360 and 420°C respectively. At the third endothermal peak appearing at 725°C , lead oxide begins to fuse.

In the d. t. a. curve of *soda* ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) a strong endothermal peak is observable at about 1400°C ; this peak represents the escape of crystal water. The small endothermal peaks appearing at 355 and 480°C , respectively, may represent inversions. The fusion of soda in the curve starts at 820°C . Its dissociation does not begin until 1400°C .

According to KAUFMANN and DILLING [73], the thermal curve of *azurite* shows up to 1000°C only one single large endothermal peak, at about 390°C .

P. WIEDEN [170] dealt with quantitative d. t. a. determination of carbonate minerals too, in the determination of magnesite, dolomite and calcite he attained an accuracy of 2 to 4%.

9. Nitrates

Among nitrates, the two most important minerals which occur in nature are sodium nitrate (NaNO_3) and potassium nitrate (KNO_3). D. t. a. is not used for the determination of these minerals, as they are easily identifiable by other methods. In their d. t. a. curves one may observe endothermal peaks corresponding to the inversion point and fusion point respectively. E. g. NaNO_3 shows an endothermal peak resulting from fusion at about 310°C , in the case of KNO_3 an endothermal peak representing inversion from one modification into another appears at 128°C , a second endothermal peak at about 340°C indicating fusion.

10. Halogenides

There are likewise very few references on the d. t. a. of halogenides, for this is not a usual method for detection of natural halogenides. In the thermal curves one may observe inversion points and fusion points. E. g. in case of halite, one single endothermal peak appears at 804°C , indicating the fusion of NaCl . The case of sylvite is similar, only that the peak marking fusion appear at a 30°C lower temperature.

The d. t. a. curve of cryolite $[\text{Na}_3(\text{AlF}_6)]$ was published by KAUFMANN and DILLING [78]. The curve shows at 570°C an endothermal peak which is reversible, being in correlation with the inversion of the cryolite modification. The curve was interrupted before 800°C , the fusion point of cryolite.

According to KAUFMANN and DILLING, a similarly small, sharp endothermal peak may be observed at about 760°C in the thermal curve of fluorite. This is followed by a broad, weak endothermal peak about at 840°C . The authors do not give the origin of the peaks.

11. Differential thermal analysis of natural organic substances

In many cases it occurs, that in the course of thermal analysis of clays or other rocks, one may observe in the thermogram an exothermal peak from 200°C on, which is not so sharp as the usually double peak of pyrite, but is broader and shows various shapes and temperatures. Exothermal peaks of this kind, appearing in the thermal curves at relatively low temperatures, are generally due to contamination with humus.

Peaks appearing at higher temperatures (500 to 600°C) may indicate a coal-bearing substance. In the case of graphite contents, the exothermal peak resulting from combustion, appears at still higher temperatures, between 700 and 800°C .

The above-mentioned phenomena only concern observations on the appearance of organic substances as accessory components in the curves. On the other hand, detailed differential thermal analyses were carried out in order to examine the behaviour of different ranks of coals.

The method of d. t. a. for coals does not deviate from those described above, only that investigations are more frequently carried out in inert atmosphere or in vacuum in this case.

H. D. GLASS [53] sought and found a correlation between the degree of coalification and d. t. a. curves of coals. His curves were not taken in an inert atmosphere or in vacuum, but by placing a loose-fitting cover on the sample holder, he obtained that after the beginning of the escape of volatiles from coal

the entry of air was inhibited, thus the coal was only surrounded by the escaping gases. In the thermal curves of the coal samples investigated, he found peaks in the following domains: 1. an endothermal peak accompanying dehydration between 120 and 150°C; 2. an exothermal peak which generally occurs after the dehydration peak, and lasts till the beginning of devolatilization, in the domain of temperature between 240 and 610°C; 3. endothermal peak or peaks resulting from devolatilization between 435 and 735°C; the number, magnitude and temperature of these peaks is one of the characteristics of the different ranks in coal. 4. A sharp endothermal peak at about 400°C, occurring in case of high-volatile coals, the cause of this peak is unknown; 5. an exothermal peak following volatile loss and resulting from structural changes taking place in the coal, this alteration results in graphitization at about 800°C; 6. an endothermal peak between 800 and 1000°C, probably caused by evolution of hydrogen.

In plate XXXVI we present the curves of GLASS on some coal types. This author pointed out, as a result of systematical investigations, that the rank in coal can be determined on the basis of d. t. a., for one may establish a correlation between the grade of coalification and the position and magnitude of the above-mentioned peaks in the curve. GLASS summed up his results in a table, the first heading of which indicates the rank of coalification, other headings indicating the different types of peaks.

W. L. WHITEHEAD and L. H. KING [173] carried out investigations on coal in a vacuum. They examined ten vitrite samples and pointed out, that there was a correlation between the temperature of the exothermal peak appearing at about 400 to 530°C and the bound carbon contents of the vitrite samples. The authors consider, that a great amount of further investigations are advisable, before drawing decisive conclusions.

Rank	Water	Low temperature exothermal	High volatile exothermal	Endothermal volatile loss	
Meta-anthracite	none	575—610			725—735
Anthracite	125—140	420—470			660—680
Semi-anthracite	130—140	250—350			630—670
Low-volatile bitum.	130—150	230—280		490—510	610—635
Medium-volatile bitum.	125—140	225—265	(455—465)	480—510	615—635
High-volatile bitum.	130—135	240—250	425—435	510—520	610—625
Subbituminous	150	260		440	570
Lignite	150	250		445	?
Peat	140	320		435	

In a recent work [54] H. D. GLASS investigated the coals, with respect to their coking ability. He pointed out, that coking coals showed three endothermal peaks, namely at about 400, 500 and 620° C. The peak actually appearing in the thermal curve of the coal and the magnitude of the three peaks compared to each other are in correlation to the coking ability of the coal. He succeeded in correlating the classification established on the basis of thermal curve with the German coking classification. His results are very clearly summed up in the following table :

German classification	Temperature and relative magnitude of thermal peaks	Characterization of coking ability
Flammkohle > 40% volatile matter	500 > 400 and! 500 = 400	Generally not well coking
Gasflammkohle ca. 40—35% V. M.	620 > 500 > 400	Only coking blended with suitable coal
Gaskohle 35—28% V. M.	400 > 500 > 620 620 < 500	Generally better coking blended
Fettkohle 28—22% V. M.	620 < 500	Well-coking
Esskohle 19—16% V. M. 16—12	620 < 500	Generally only coking blended with suitable coal

W. J. SMOTHERS and Y. CHIANG [156] give an account of thermal investigations on lignites. They have observed several endothermal and exothermal peaks in the thermograms of same. In order to determine the character of the processes resulting in the respective peaks, they performed their experiments in air, oxygen and nitrogen, furthermore they investigated preheated lignite samples, too. There were some differences between the shapes and magnitudes of the peaks of different kinds of lignite. At the beginning of the thermal curve of lignite an endothermal peak resulting from the escape of moisture was observed at about 110° C. The first exothermal peak appeared at about 300° C, where decompositions accompanying oxidation were taking place in the lignite, in the course of evolution of CO₂ and CO gases. This process requires a small amount of oxygen, but it does not take place if the entry of oxygen is totally inhibited. The second exothermal peak usually appears at about 600° C, it results from the combustion of organic substance, accompanied by the evolution of CO₂ gas. In case of experiments carried out in nitrogen or vacuum, the latter peak did not appear. Thereafter, the lignite curve shows a high-temperature endothermal peak, which is particularly distinct, if the investigation is carried out in nitrogen. This endothermal process is accompanied by considerable gas formation, which obviously consists of volatiles escaping at high temperatures. Between 800 and 900° C further oxidation process again results

in an exothermal peak. For comparison, the authors give an exposition on the d. t. a. curves of humus acid and lignin, too.

Recently, Hungarian researchers have also carried out investigations on this subject. Systematical thermal investigations of coal were initiated by PAULIK and his collaborators [136]. Besides d. t. g. curves they were also taking d. t. a. curves. In their first publication they give account of investigations performed on peats and components of peat. In plate XXXVI/c we present one of their d. t. a. records of peat and, for comparison, a d. t. g. curve of spruce.

It follows that d. t. a. has fair prospects concerning coal analyses, in respect to qualitative characterization and classification of coals.

PART III

Application of differential thermal analysis in practice and science

1. *In geological research*

The role of d. t. a. in geological research has become more and more important. On one hand this method is quick enough to follow the course of investigation, on the other hand a simplified form of the required apparatus is suitable for taking measurements in fields, too. Such a solution was proposed by S. B. HENDRICKS, S. S. GOLDRICH, and R. A. NELSON [72] as early as 1946. Let us now see the raw materials, in the prospecting and mining for which d. t. a. can be well utilized. First of all, one may take bauxite prospection and mining into consideration where the presence and even the amount of the various minerals can be controlled in the course of investigation. At the Hungarian State Geological Institute we already have carried out systematical d. t. a. investigations of several Hungarian bauxite occurrences, e. g. 58 samples taken, following the strata of the section of the occurrence of Nagyharsány, the occurrences of Iszkaszentgyörgy and Nézsa. We have also published a paper on the investigations of the latter occurrences [43].

D. t. a. is very useful in refractory clay investigation and mining, too. Quantitative determination of kaolinite is also feasible with sufficient accuracy, consequently one may continuously control the changes in quality of refractory clay in the course of extraction.

In the bentonite industry, the application of this method is of less success. In consequence of causes exposed in Part II, quantitative determinations of clay minerals belonging to the montmorillonite and illite groups do not give satisfactory data, therefore d. t. a. is only suitable for informative, qualitative investigations on this terrain. Notwithstanding, results of d. t. a., in bentonite investigation, give very valuable informations on the mineral components of bentonite.

D. t. a. is applicable to gypsum investigation too, there it has the principal advantage of proving suitable for the distinction of gypsum and anhydrite.

D. t. a. can render service in the investigation and mining of manganese too. E. g. it is difficult to identify carbonate manganese ore in field, consequently it often occurred, that carbonate manganese ore was put aside as refuse. This ore is traceable on the spot by the help of d. t. a.

Finally, d. t. a. is applicable to coal investigations, particularly in classification of coal rank, although in this terrain the investigations are as yet not to be considered as conclusive, and in practice the application of this method still requires considerable research work.

In geology, d. t. a. can be applied not only in practical investigations, but to solve theoretical problems too. It is applied, for the most part, for genetical problems of clay minerals and bauxite minerals, parallelly with X-ray and electron microscopic investigations. In the course of our own investigations, we have many times tried to decide the identity or dissimilarity of several strata by d. t. a. This method is also applied to diagnose new minerals, a case in point, is huntite or dillnite, which was recently determined as a homogeneous mineral.

2. In soil science

Since the importance of clay minerals had been recognized in the classification of soils, d. t. a. became a method for soil investigation, besides X-ray investigations. By means of d. t. a. one can not only characterize different sorts of soils, but this method also furnishes important data concerning genetical problems of soils. The importance of the results obtained by d. t. a. is proved by a great number of scientific papers [4, 27, 55, 115].

3. In silicate industry

Apart from the fact that raw materials for production are naturally testable by d. t. a., this method plays a special role in silicate industry, concerning the elucidation and control of the mechanism of manufacturing processes. E. g. R. BARTA and VL. SATAVA [8] emphasize the importance of d. t. a. in cement industry. First of all, by this method one can follow the process of lime kilning. In this respect, the above-mentioned authors have pointed out, that old experts of lime industry were mistaken when they were of the opinion that lime kilning was facilitated by adding NaCl. It was demonstrated by d. t. a. investigations, that dissociation heat of calcium carbonate did not decrease by adding NaCl. Farther the authors have used d. t. a. for controlling calcium hydrates. The method can render service in following the mechanism of cement setting,

it is also possible to observe the effect of various additive agents in the process of cement setting, by d. t. a. Naturally, these examinations are only practicable by equipments suitable for corresponding high temperature measurements. D. t. a. may be applied to control the contraction and consolidation of cement, too.

The utilization of d. t. a. in the cement industry has also been introduced in Hungary [161].

D. t. a. is the most widely applied in ceramic industry. It plays a decisive part in raw material testing, in this same industry, but it can be used in different phases of the manufacturing process. In the technical journals of ceramic industry one can find a great number of scientific publications on various applications of this method.

Many recent Hungarian references also prove that d. t. a. is employed in ceramic industry. We have to mention here the papers by GROFCSIK and VÁCÓ [64, 65], further on a paper by T. TAKÁCS [163] who has carried out X-ray and d. t. a. investigations on ceramic raw materials from Hegyalja (North Hungary), and by means of these investigations and oxidation analyses of the samples he has given, by computing, the quantitative mineral composition of the samples.

There are some references on the thermal investigation of silicate glasses too [164, 30].

4. In industrial hygiene

In this discipline, many papers were recently published, which gave account of the application of d. t. a. to investigations carried out, in order to prevent silicosis [113, 92]. Scil. it is known that determination of free quartz by d. t. a. is practicable, even in the presence of other silicates. However, since it has been pointed out that the peak marking the inversion of quartz was relatively small, one must choose an apparatus of higher sensitivity than the usual one, in order to make quantitative determinations more accurate. A. KÖHLER and P. WIEDEN [92] succeeded in increasing the sensitivity of their apparatus, employed for the determination of free quartz content of rocks, to such a degree that they could carry out unequivocally the quantitative determination of less than 1% quartz content, and could even detect the presence of 0.1% quartz.

5. Application of d. t. a. to thermochemical problems

From the thermal curve — as has been seen — two data are obtained concerning the peaks. The first one is the peak temperature, the second the magnitude of peak deflection or rather the extent of the peak area. The former

is principally used for identification, qualitative determination of the mineral substance, the latter, as is known, is suitable also for the quantitative determination of the mineral present. However, both data may lead to further scientific conclusions. Namely, one may infer from peak temperatures, in case of compounds of identical types, relative stabilities (e. g. the stability of CaCO_3 if higher than that of MgCO_3 , the latter dissociates at about 200° lower temperature). However, the conclusion which can be drawn from measuring the peak areas, is much more important. I. e. by means of this datum, in the case of a given amount of substance, the heat absorbed or produced in the course of the processes of alteration, dissociation etc. could be determinable.

As has been already mentioned, one could read as early as the twenties of this century, the papers by KURNAKOV and his collaborators in which they proposed to infer lattice energies from d. t. a. curves.

In 1951, WITTELS suggested the application of d. t. a. as micro-calorimeter in such a way, that he calibrated the extent of the peak area by substances of known decomposition heat [175]. He points out that the peak area corresponding to one thermal unit, decreases in proportion to the rise in temperature, further on he demonstrates that in the case of a higher heating rate peak areas become larger. The same phenomenon was mentioned in the description of our "rapid" apparatus.

In 1952, BARSHAD [6] calibrated his d. t. a. curves under 200°C by organic substances of known fusion heat, over 200°C by inorganic compounds of known fusion heat or decomposition heat, and by means of these calibration-data he obtained well concordant data concerning various minerals which contained OH radicals.

SABATIER, in a paper published in 1954 [147] even more thoroughly deals with the same problem. He tries to elucidate the practicability in principle of this method, then he establishes a standard curve which gives correlation between the heat per peak area unit and the peak temperature. He demonstrates the application of this method to some minerals containing OH.

If one compares the results of various authors, these results are not concordant. Consequently, this method can not be considered as fully developed, and requires further development.

According to the proposal of KULP and his collaborators [99], the values of heat formation determined on the basis of thermal curves may be used for the determination of the geological age, too. Metamict minerals are suitable for this kind of determination, for they recrystallize during heating. In the case of minerals cited as instance (metamict zircon, metamict samarskite etc.) recrystallization results either in a one-step or in a two-step endothermal peak. The more troubled the structure of the metamict mineral (i. e. the more intensive the radioactivity absorbed), the larger the peak. It follows, that in case of given radioactivity, the longer the mineral was exposed to radioactivity, the larger

the exothermal peak marking recrystallization. Consequently if, besides the magnitude of the above-mentioned peaks, the intensity of radioactivity of the sample is also determined, the age of the mineral can be reckoned from the two data.

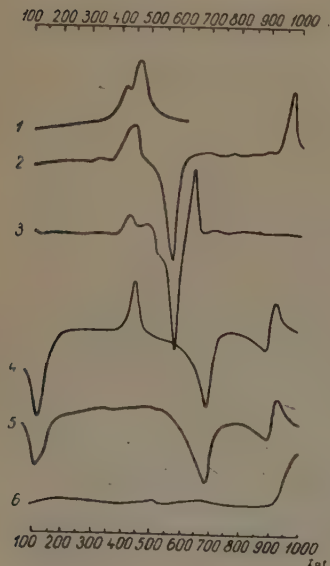
The latter applications of differential thermal analysis are to be considered as prospects, rather than a developed method, however new and important results in the course of future evolution of this method is to be expected, in this very direction.

Plate I/a

Thermograms of sulfides

1. Double pyrite peak (SOVERI) (157)
2. Pyritiferous kaolin, Mountain of Velence, Hungary (Hungarian State Geological Institute, Budapest, 1954)
3. Pyritiferous siderite, Rudabánya, Hungary (Hungarian State Geological Institute, Budapest, 1954)
4. Wyoming bentonite + 1% pyrite, in air (ROWLAND and LEWIS) (143)
5. Wyoming bentonite + 1% pyrite, in nitrogen (ROWLAND and LEWIS [143])
6. Sphalerite, Joplin, Missouri (KAUFMANN and DILLING) (78)

Plate I/b

Thermograms of sulfides in nitrogen according to HILLER and PROBSTHAIN (74)

1. Pyrite
2. Chalcopyrite
3. Covelline
4. Covelline in air
5. Antimonite
6. Argentite

Plate II

Quartz curves

1. Quartz, Ottawa, Illinois (GRIM and ROWLAND) (62)
2. Quartz, Hot Springs, Arkansas (FAUST) (37)
3. Quartz, Mt. Asztaghegy, Gyöngyössólymos, Hungary (Hungarian State Geological Institute, Budapest, 1953)
4. Quartz, Máramaros, Roumania (Hungarian State Geological Institute, Budapest, 1953).
5. Quartz beside kaolin, Bánk, Hungary (Hungarian State Geological Institute, Budapest, 1954).
6. Quartz beside montmorillonite, Végardó, Hungary (Hungarian State Geological Institute, Budapest, 1955).

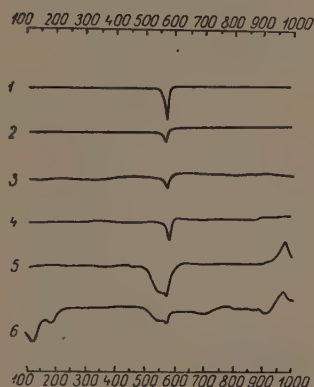


Plate III

Thermograms of manganous oxides

1. Pyrolusite, Nova Scotia (Hungarian State Geological Institute, Budapest, 1954).
2. Ramsdellite, Idorado mine, Colorado (KULP and PERFETTI) (97).
3. Hausmannite, Ilmenau, Thüringen (KULP and PERFETTI) (97)
4. α hausmannite (RODE) (137)
5. Braunite, Thüringen (KULP and PERFETTI) (97)
6. MnO_2 , prepared artificially by GRASSELLY (Hungarian State Geological Institute, Budapest, 1955)
7. Mn_2O_3 , prepared artificially by GRASSELLY (Hungarian State Geological Institute, Budapest, 1955)
8. Mn_3O_4 , prepared artificially by GRASSELLY (Hungarian State Geological Institute, Budapest, 1955)

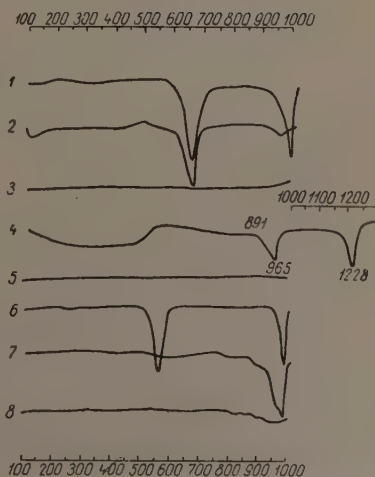
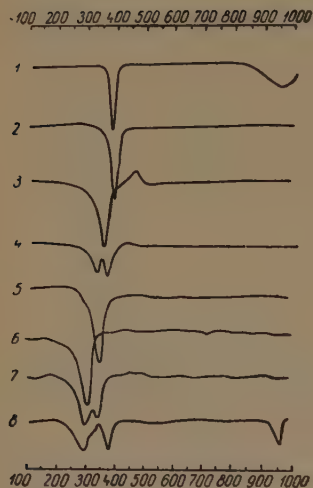
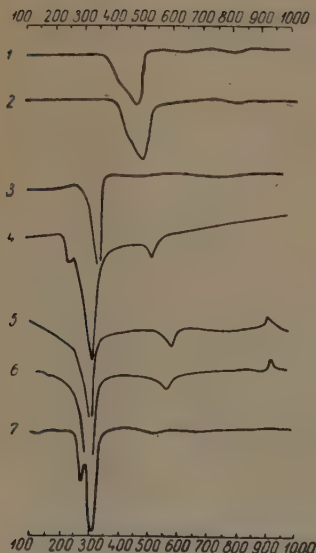


Plate IV

Thermograms of iron oxides and manganite

1. Manganite, Ilfeld (KULP and PERFETTI) (97)
2. Goethite, Cornwall (KULP and PERFETTI) (97)
3. Lepidocrocite, Northampton, Pa. (KULP and TRITES) (98)
4. Artificial mixture of 60% lepidocrocite and 40% goethite (KULP and TRITES) (98)
5. Goethite, Rudabánya, Hungary (Hungarian State Geological Institute, Budapest, 1954)
6. Lepidocrocite, Meszes, Hungary (Hungarian State Geological Institute, Budapest, 1955)
7. Lepidocrocite and goethite, Tornaszentandrás, Hungary (Hungarian State Geological Institute, Budapest, 1955)
8. Artificial mixture of lepidocrocite and manganite

Plate V

Thermograms of Mg and Al hydroxides

1. Brucite, Brewster (KAUFFMAN and DILLING) (78)
2. Brucite (NORTON) (127)
3. Hydrargillite, Istria (Hungarian State Geological Institute, Budapest, 1953)
4. Artificial hydrargillite (ERDEY and PAULIK) (33)
5. Bauxite, Iszka-szentgyörgy, Hungary (M. FÖLDVÁRI-VOGL) (41)
6. Bauxite, Halimba (VACHTL) (166)
7. Bayerite (KAUFMANN and DILLING) (78)

Plate VI

Thermograms of aluminium oxy-hydroxides

1. Diaspore, Chester, Massachusetts (BRADLEY and GRIM) (17)
2. Boehmite (SPEIL, BERKELHAMER, PASK, DAVIES) (159)
3. Bauxitiferous Eocene clay, Gánt, Hungary (M. FÖLDVÁRI—VOGL) (41)
4. Bauxite, Markušovce, CSR. (KONTA) (88)
5. Bauxite, containing diaspore, Nézsa, Hungary (M. FÖLDVÁRI—VOGL) (41)
6. Bauxite, containing hydrargillite and boehmite, Nagynémetegyháza, Hungary (M. FÖLDVÁRI—VOGL) (41)

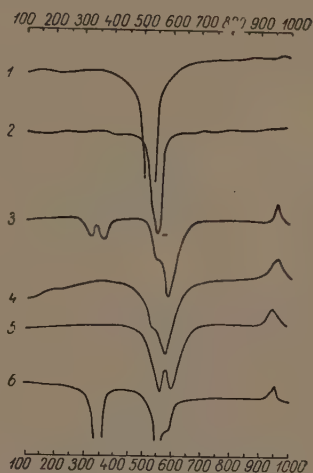


Plate VII

Thermograms of tourmalines (according to KURYLENKO) (103)

1. Black tourmaline, St. Gotthard (Switzerland)
2. Black tourmaline, Brazil
3. Black tourmaline, Madagascar
4. Black tourmaline, Madagascar (decomposed sample)
5. Colourless tourmaline, Elba
6. Dravite, rich in Mg, Czechoslovakia
7. Rubellite, San Diego, USA

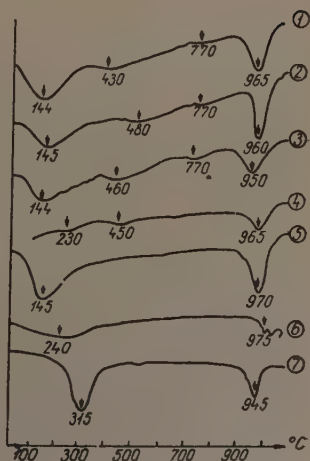
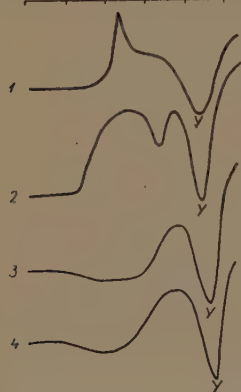


Plate VIII/a*Thermograms of amphiboles (according to WITTELS) (177)*

600 700 800 900 1000 1100



1. Tremolite

2. Richterite

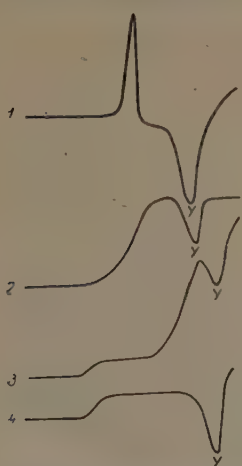
3. Na-tremolite, glaucophane

4. Na-tremolite, glaucophane

600 700 800 900 1000 1100

Plate VIII/b*Thermograms of amphiboles (according to WITTELS) (177)*

600 700 800 900 1000 1100



1. Anthophyllite (high Mg content)

2. Anthophyllite (high Fe content)

3. Hastingsite

4. Pargasite

600 700 800 900 1000 1100

Plate IX

Thermograms of sepiolite

1. Ampandrandava (CAILLÈRE) (21)
2. Madriat, Sistrière (CAILLÈRE) (21)
3. New Mexico (KAUFFMAN and DILLING) (78)
4. Beto County, Md. (KERR, KULP, HAMILTON) (82)
5. Spain (KERR, KULP, HAMILTON) (82)
6. Meerschaum, Turkey (KERR, KULP, HAMILTON) (82)

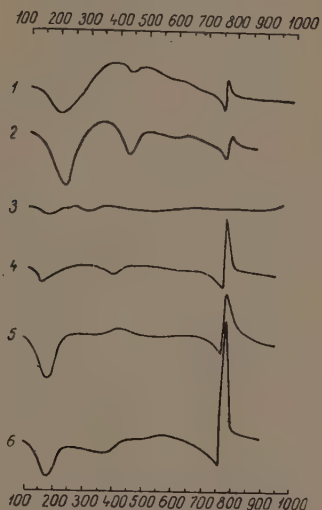


Plate X

Thermograms of paligorskite (attapulgit)

1. Maevatanana (CAILLÈRE) (21)
2. Le Vigan (CAILLÈRE) (21)
3. Attapulgit, Quincy, Florida (GRIM and ROWLAND) (62)
4. Attapulgit, Georgia (KERR, KULP and HAMILTON) (82)
5. Attapulgit, Georgia (KERR, KULP and HAMILTON) (82)
6. Attapulgit, Quincy, Florida (KERR, KULP and HAMILTON) (82)

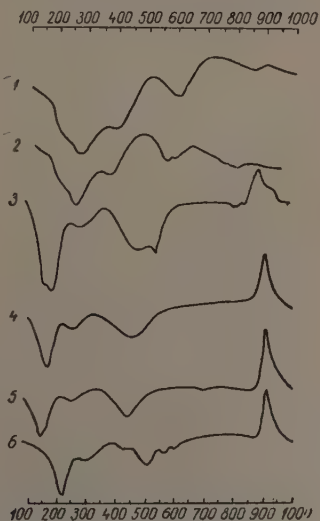
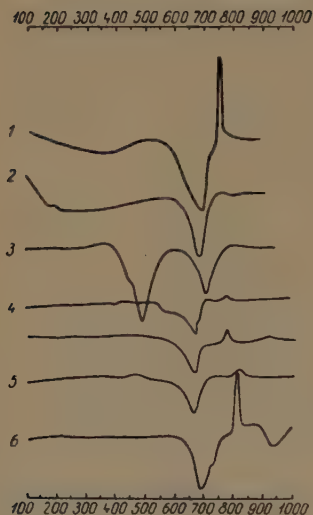
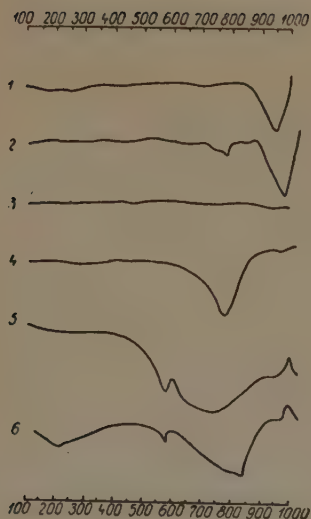


Plate XI

Thermograms of serpentine minerals

1. α antigorite (CAILLÈRE) (21).
2. β antigorite (CAILLÈRE) (21)
3. β antigorite (CAILLÈRE) (21)
4. Serpentine, New York (KAUFFMAN and DILLING) (78)
5. Serpentine, Coos County (KAUFFMAN and DILLING) (78)
6. Serpentine, Perkupa, Hungary (Hungarian State Geological Institute, 1955)

Plate XII

Thermograms of talc and pyrophyllite

1. Talc, Vermont (GRIM and ROWLAND) (62)
2. Talc, Felsőcsatár, Hungary (Hungarian State Geological Institute, 1955)
3. Pyrophyllite (NORTON) (127)
4. Pyrophyllite, North Carolina (GRIM and ROWLAND) (62)
5. Pyrophyllite, Robbins, N. C. (KERR, KULP and HAMILTON) (82)
6. Pyrophyllite, Robbins, N. C. (KERR, KULP and HAMILTON) (82)

Plate XIII

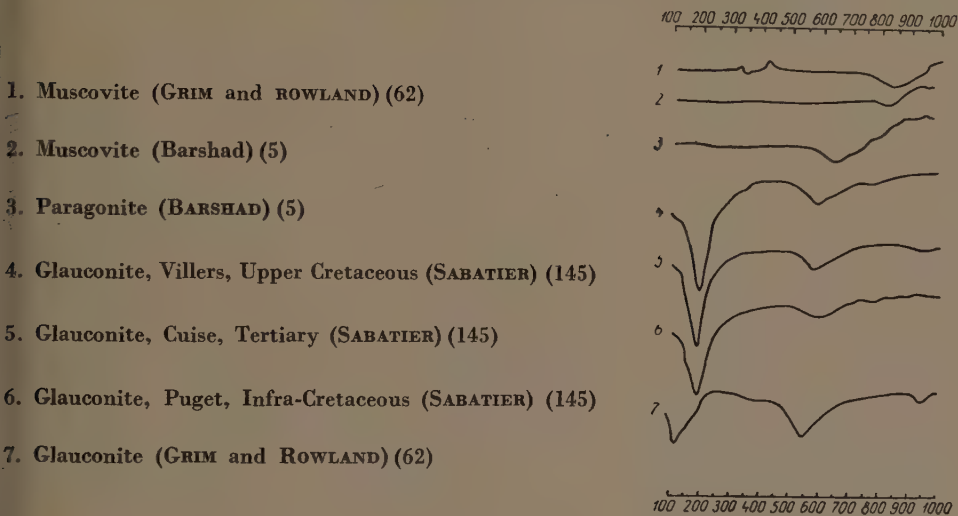
Thermograms of micas

Plate XIV

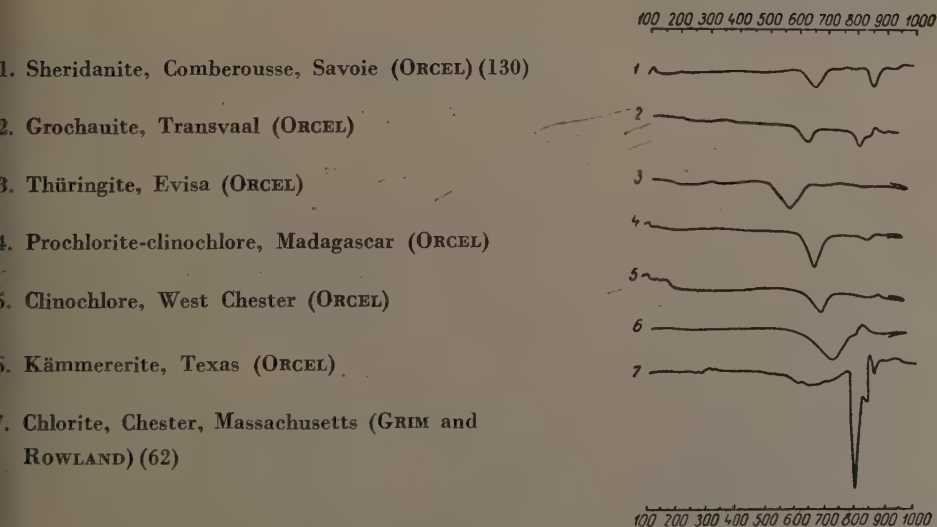
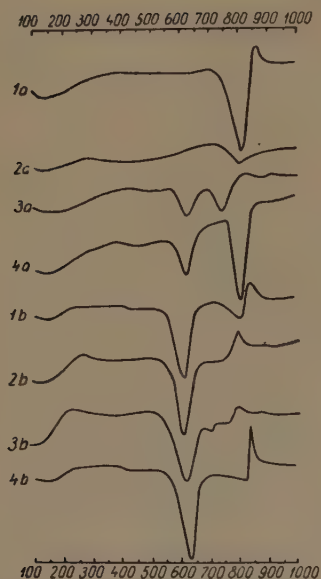
Thermograms of chlorites

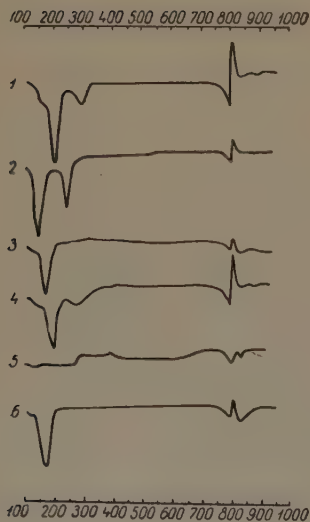
Plate XV

Thermograms of chlorites (according to SABATIER) (146)

1a, 2a, 3a, 4a coarse-grained chlorite samples

1b, 2b, 3b, 4b the same chlorite samples after fine powdering

Plate XVI

Thermograms of vermiculites (according to BARSHAD) (5)

1. Natural vermiculite

2. Vermiculite saturated with Ca

3. Vermiculite saturated with Na

4. Vermiculite saturated with Mg (re-altered from vermiculite previously saturated with Na, into Mg-vermiculite)

5. Vermiculite saturated with NH_4

6. Vermiculite saturated with K

Plate XVII

Thermograms of feldspars (according to A. KÖHLER and P. WIEDEN) (91)

1. Albite, Rischuna, Switzerland
2. Oligoclase, Tvedestrand, Norway.
3. Labradorite, Labrador
4. Anorthite, Pesmeda, Italy
5. Anorthite, Kanatsuki, Japan

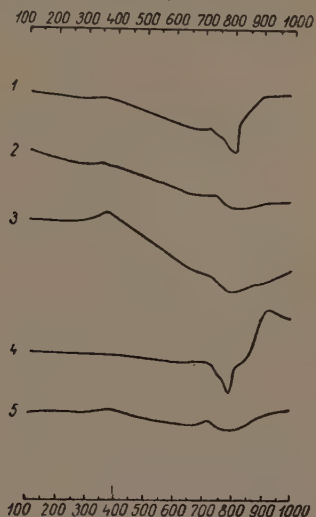


Plate XVIII

Thermograms of kaolinites

1. Kaolinite, Zettlitz (Hungarian State Geological Institute, 1953)
2. Kaolinite, Pilisvörösvár, Hungary (Hungarian State Geological Institute, 1953)
3. Kaolinite, Budakeszi-Hárshegy, Hungary (Hungarian State Geological Institute, 1954)
4. Kaolinite, Végardó, Hungary (Hungarian State Geological Institute, 1955)
5. Kaolinite, Langley (GRUVER, HENRY, HEYSTEK) (68)
6. Kaolinite, Langley + 6% NaCl (GRUVER, HENRY, HEYSTEK) (68)
7. Kaolinite, Langley + 10% Na₂CO₃ (GRUVER, HENRY, HEYSTEK) (68)

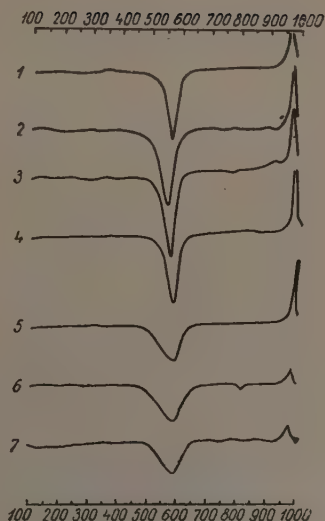
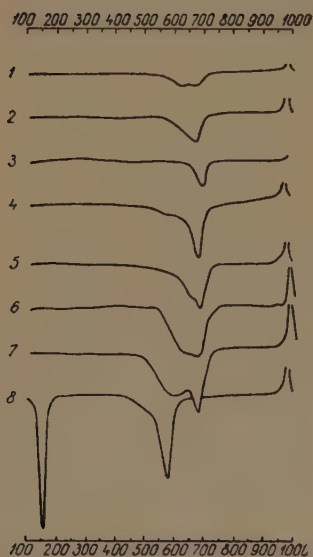
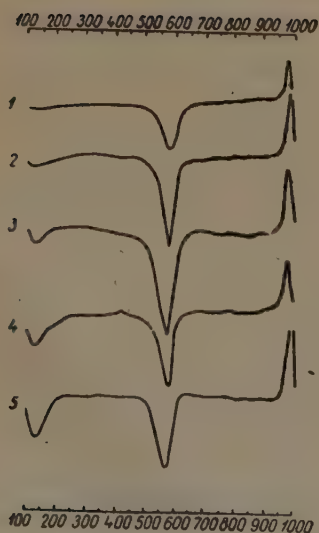


Plate XIX

Thermograms of minerals of the kaolin group

1. Nacrite (NORTON) (127)
2. Nacrite, Freiberg (JASMUND) (76)
3. Dickite (NORTON) (127)
4. Dickite, Colorado (KERR, KULP, HAMILTON) (82)
5. Dickite and nacrite together, St. George, Utah (KERR, KULP, HAMILTON)
6. Nacrite and dickite together, Mád, Hungary (Hungarian State Geological Institute, 1954)
7. Dickite and nacrite together, Zsolnay mine, Sárospatak, Hungary (Hungarian State Geological Institute, 1953)
8. Halloysite, Djebel Debar, Algiers (JASMUND) (76)

Plate XX



*Thermograms of kaolin minerals of Szegilong
(Hungarian State Geological Institute, 1955)*

Plate XXI

Thermogram of montmorillonites
Variation of exchangeable cation (according to BARSHAD) (7)



Plate XXII

Thermograms of montmorillonites

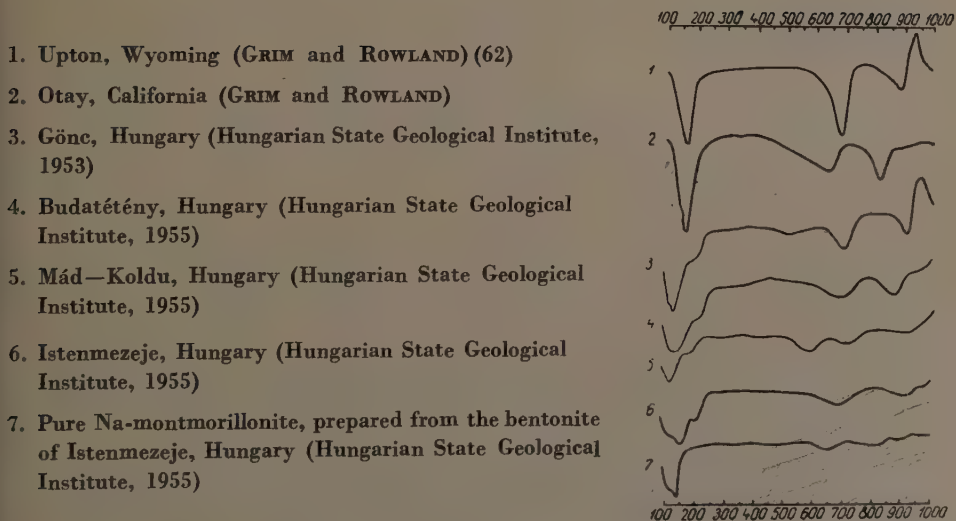
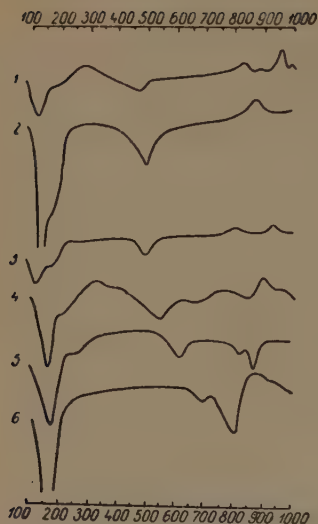
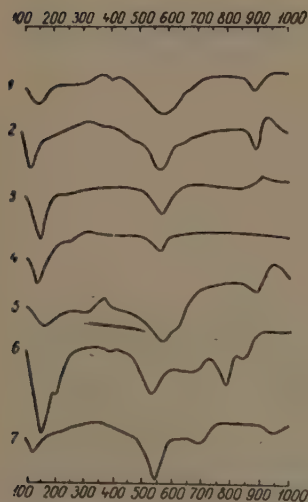


Plate XXIII

Thermograms of nontronite, beidellite and hectorite

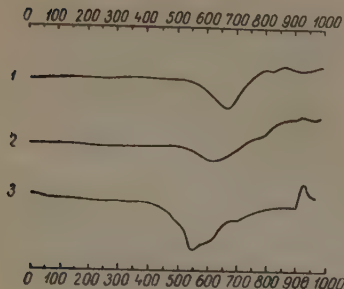
1. Nontronite, San Luis, Potosi, Mexico (GRIM and ROWLAND) (62)
1. Nontronite, Manito, Washington (KERR, KULP, HAMILTON) (82)
3. "Chloropal", Uzhgorod, USSR, (Hungarian State Geological Institute, 1955)
4. Beidellite, Beidell, Colorado (GRIM and ROWLAND) (62)
5. Saponite, Cornouailles (CH. KIEFER) (83)
6. Hectorite, Hector, California (KERR, KULP, HAMILTON) (82)

Plate XXIV/a

Thermograms of illites

1. Illite, Alexander County, Illinois (GRIM and ROWLAND) (62)
2. Illite, Vermilion County, Illinois (GRIM and ROWLAND) (62)
3. Pleistocene clay, Solt, Hungary (M. FÖLDVÁRI-VOGL) (42)
4. Pleistocene clay, Vámosgyörk, Hungary (M. FÖLDVÁRI-VOGL) (42)
5. Quaternary soil of Sweden (F. WIKLANDER) (174)
6. Illite and montmorillonite, Pioche, Nevada (KERR, KULP, HAMILTON) (82)
7. Illite, Sárospatak (more precisely Füzérradvány) Hungary (GRIM and ROWLAND)

Plate XXIV/b

Thermograms of hydromicas

1. Hydromuscovite, Nagybörzsöny, Hungary (J. ERDÉLYI) (35); (Hungarian State Geological Institute, 1956)
2. Paragonite (BARSHAD) (5)
3. Hydromuscovite? (leverrierite), Lukavice (KONTA) (90)

Plate XXV

Thermograms of mixtures of illite and kaolinite (according to GRIM and ROWLAND) (62)

1. 95% illite and 5% kaolinite
2. 90% illite and 10% kaolinite
3. 75% illite and 25% kaolinite
4. 50% illite and 50% kaolinite
5. 25% illite and 75% kaolinite
6. 10% illite and 90% kaolinite

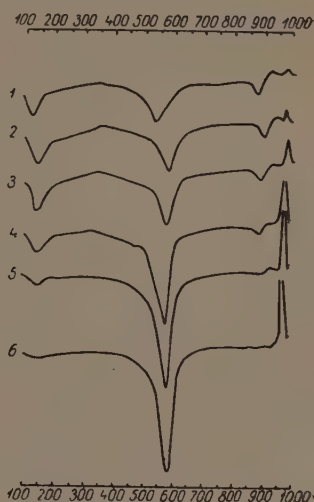


Plate XXVI

Thermograms of mixtures of various clay minerals

1. 50% Ca-montmorillonite and 50% kaolinite (GRIM) (58)
2. 75% Na-montmorillonite and 25% illite (GRIM and ROWLAND) (62)
3. 25% Na-montmorillonite and 75% illite (GRIM and ROWLAND) (62)
4. Kaolinite, Na-montmorillonite, illite (1 : 1 : 1) (GRIM)
5. Kaolinite, Na-montmorillonite, illite (3 : 1 : 1) (GRIM)

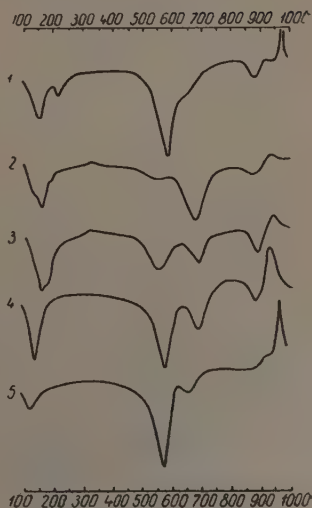
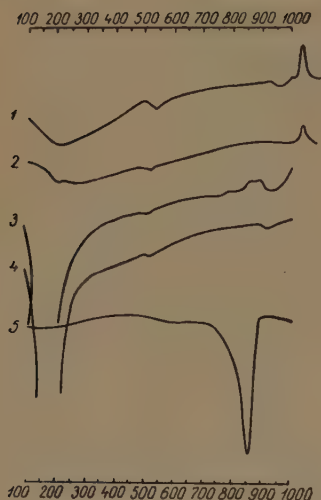


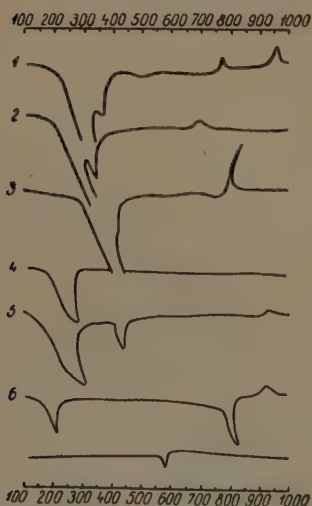
Plate XXVII

Thermograms of allophane and dillnite



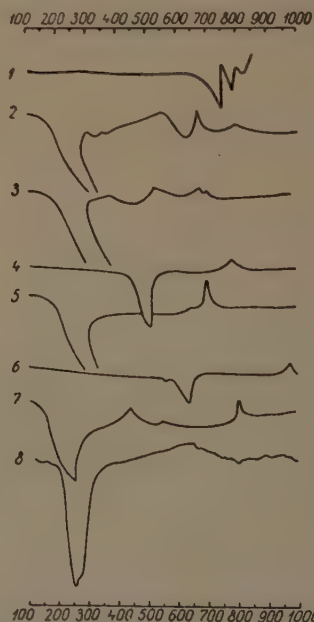
1. Rose allophane*, Lawrence County, Indiana (WHITE) (171)
2. Vitreous allophane*, Lawrence County, Indiana (WHITE)
3. Rose allophane, in natural state of moisture
4. Vitreous allophane, in natural state of moisture
5. Dillnite, Banská Belá, Czechoslovakia (KONTA) (89)

Plate XXVIII/a

Thermograms of phosphates
(according to R. L. MANLY) (117)

1. Zepharovichite (?) Czechoslovakia — 2. Wavellite, Montgomery, Arkansas — 3. Turquois, New Mexico — 4. Variscite, Fairfield, Utah — 5. Bolivarite, Ponte Verde, Spain — 6. Lazulite, Georgia — 7. Berlinite (artificial mineral)

Plate XXVIII/b

Thermograms of phosphates
(according to R. L. MANLY) (117)

1. Amblygonite, Black Hills, Dakota — 2. Vivianite, Keystone, Dakota — 3. Bobierite, Edgerton, Minnesota — 4. Wardite, Lewiston, Utah — 5. $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (artificial) — 6. Augelite, Laws, California — 7. Evansite, Goldberg, Idaho — 8. Kingite (NORRISH, ROGERS, SHAPTER) (126)

* These samples were investigated after previous heating up to 140°C

Plate XXIX

Thermograms of phosphates (according to CVETKOV and VALYASHINA) (26)

1. Thenardite
2. Glauberite
3. Baryte
4. Anglesite
5. Anhydrite
6. Coelestine

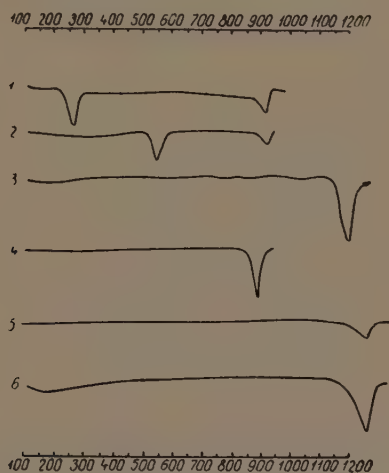


Plate XXX

Thermograms of alunite and jarosites

1. Alunite, Santa Rita, New Mexico (KULP and ADLER) (92)
2. Alunite, Nevada (KAUFFMAN and DILLING) (78)
3. Jarosite, Los Lamentos, Mexico (KULP and ADLER)
4. Jarosite, artificial (CVETKOV and VALYASHINA) (26)
5. Plumbojarosite, Almada, Mexico (KULP and ADLER) (93)
6. Argentojarosite, Eureka, Utah (KULP and ADLER)

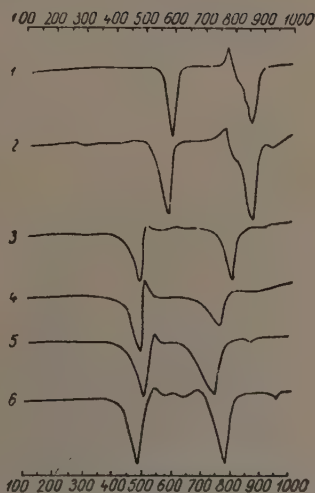
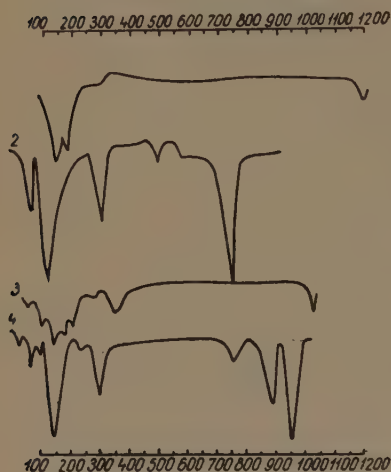


Plate XXXI/a

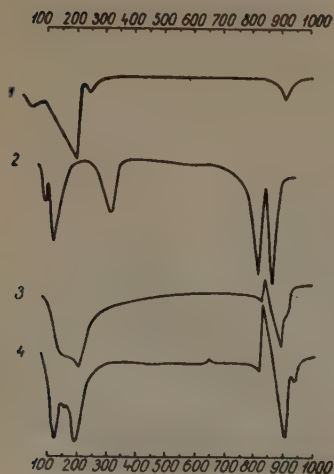
Thermograms of hydrous sulfates (according to CVETKOV and VALYASHINA) (26)



1. Gypsum
2. Melanterite
3. Epsomite
4. Goslarite

Plate XXXI/b

Thermograms of hydrous sulfates (according to CVETKOV and VALYASHINA) (26)



1. Mirabilite
2. Chalcantithite
3. Aluminite
4. Aluminite, Gánt, Hungary (GEDEON—KLIBURSZKY)
(Mineralogical-Petrographical Department of the
R. Eötvös University, Budapest)

Plate XXXII

Thermograms of carbonates

1. Calcite (KULP, KENT and KERR) (94)
2. Aragonite (FAUST) (38)
3. Magnesite (KULP, KENT and KERR)
4. Ironiferous magnesite with calcite impurity (KULP, KERR and KENT)
5. Dolomite, Nyirád—Cserhegy, Hungary (M. FÖLDVÁRI-VOGL, V. KOBLENCZ) (46)
6. Mixture of CaCO_3 and MgCO_3 (in proportion corresponding to the composition of dolomite No. 5.) (M. FÖLDVÁRI-VOGL, V. KOBLENCZ) (46)
7. Dolomite of Nyirád-Cserhegy + 5% KCl (M. FÖLDVÁRI-VOGL, V. KOBLENCZ)

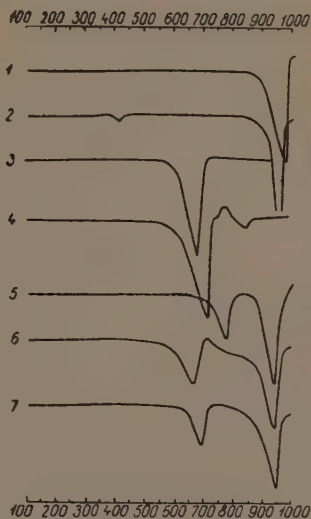


Plate XXXIII

Thermograms of carbonates

1. Siderite, Waldstein, Carinthia (KULP, KENT and KERR) (94)
2. Siderite, Rudabánya, Hungary (Hungarian State Geological Institute, 1955)
3. Ankerite, Eisenertz, Styria (KULP, KENT and KERR)
4. Rhodochrosite, Colorado (KULP, WRIGHT and HOLMES) (100)
5. Rhodochrosite, Urkut, Hungary (Hungarian State Geological Institute, 1954)
6. Mixture of 50% rhodochrosite and 50% siderite (M. FÖLDVÁRI-VOGL, V. KOBLENCZ) (47)

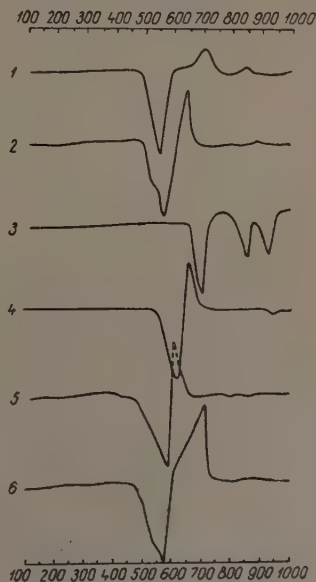


Plate XXXIV

Thermograms of carbonates

100 200 300 400 500 600 700 800 900 1000



100 200 300 400 500 600 700 800 900 1000

1. Strontianite, Hamm, Westfalen (GRUVER) (67)

2. Witheritem Northumberland, England (GRUVER)

3. Cerussite, New Mexico (Gruver)

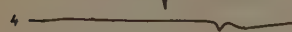
4. Soda (artificial) (GRUVER)

5. Azurite, Utah (KAUFFMAN and DILLING) (78)

Plate XXXV

Thermograms of some natural nitrates and halogenides

100 200 300 400 500 600 700 800 900 1000



100 200 300 400 500 600 700 800 900 1000

1. Sodium nitrate (BARSHAD) (6)

2. Sodium chloride (BARSHAD)

3. Cryolite, Groenland (KAUFFMAN and DILLING) (78)

4. Fluorite, Tennesco (KAUFFMAN and DILLING)

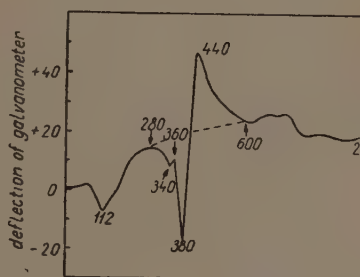
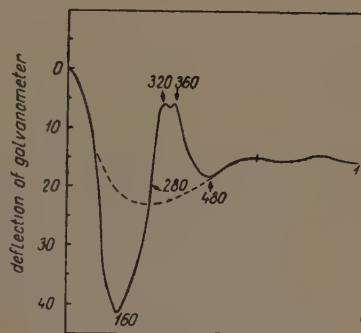
Plate XXXVI/a*Thermograms of coals (according to GLASS) (53)*

1. Meta-anthracite (1,8% V. M.)

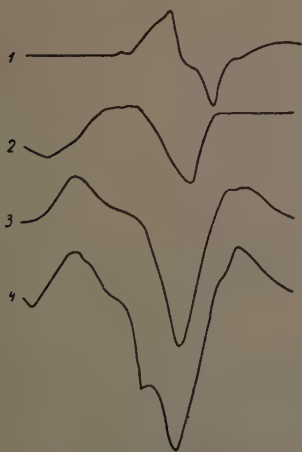
2. Anthracite (2,3% V. M.)

3. Semi-anthracite (8,0% V. M.)

4. Bituminous coal (15,9% V. M.)

**Plate XXXVI/b***Thermograms of coals (according to GLASS) (52)*

100 200 300 400 500 600 700 800 900 1000

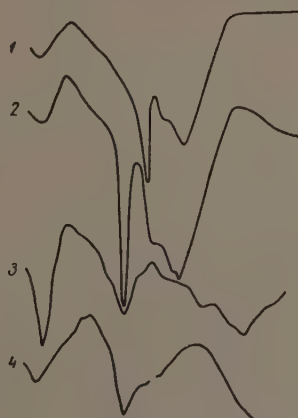


100 200 300 400 500 600 700 800 900 1000

1. Bituminous coal (24,0% V. M.) — 2. Bituminous coal (30,5% V. M.) — 3. Lignite. —
4. Peat

Plate XXXVI/c*Thermograms of peat and spruce (according to PAULIK and WELTNER) (135)*

100 200 300 400 500 600 700 800 900 1000



100 200 300 400 500 600 700 800 900 1000

1. Peat, Feketebészény, Hungary
2. Spruce

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ROLLE DER DIFFERENTIAL-THERMOANALYSE IN DER MINERALOGIE UND IN DER GEOLOGISCHEN SCHÜRFUNG NACH MINERALISCHEN ROHSTOFFEN

Von

Frau M. FÖLDVÁRI-VOGL

Synoptische Abhandlung, die einerseits zur Anwendung der Differential-Thermoanalyse in der Mineralogie und in der Geologie Richtlinien zu geben wünscht, andererseits aber die bisher in Ungarn erzielten Ergebnisse zusammenfaßt.

Im ersten Teil der Abhandlung legt die Verfasserin die theoretischen Grundlagen des Verfahrens dar und gibt die Beschreibung der bei der Differential-Thermoanalyse angewendeten Apparatur. Die durch die Verfasserin und ihre Mitarbeiter an den Apparaten durchgeführten Änderungen werden besonders hervorgehoben.

Der zweite, umfangreichste Teil des Werkes behandelt die DTA-Untersuchung verschiedener Minerale. Die Minerale werden in ein mineralogisches System gruppiert behandelt. Bei den einzelnen Kurventypen wird die Aufmerksamkeit auch auf die eventuellen Anomalien gelenkt. Die gesammelten Erfahrungen werden an ungarischen Beispielen dargestellt.

Der abschließende Teil der Arbeit befaßt sich kurz mit der anderweitigen praktischen Anwendung der DTA-Methode.

Die im Text angeführten zahlreichen DTA-Kurven erleichtern den Geologen die Identifizierung der Minerale.

РОЛЬ ДИФФЕРЕНЦИАЛЬНО-ТЕРМИЧЕСКОГО АНАЛИЗА В МИНЕРАЛОГИИ
И В ГЕОЛОГИЧЕСКОЙ РАЗВЕДКЕ НА МИНЕРАЛЬНЫЕ СЫРЬЯ

М. ФЭЛЬДВАРИ-ФОГЛ

Сводная работа, которая с одной стороны дает указания к применению дифференциально-термического анализа в минералогии и геологии, а с другой — суммирует полученные до сих пор в Венгрии результаты.

В первой части работы автор излагает теоретические основы методы, а затем приводит описание примененной для дифференциально-термического анализа аппаратуры. Особо описываются приборы, сконструированные автором и ее сотрудниками.

Вторая, наиболее пространная часть работы занимается дифференциально-термическим анализом отдельных минералов. Минералы обсуждаются по минералогическим группам. В связи с отдельными типами кривых автор обращает внимание и на возможные аномалии. Накопившиеся опыты демонстрируются на венгерских примерах.

Заключательная часть работы вкратце излагает другие возможности практического использования дифференциально-термического анализа.

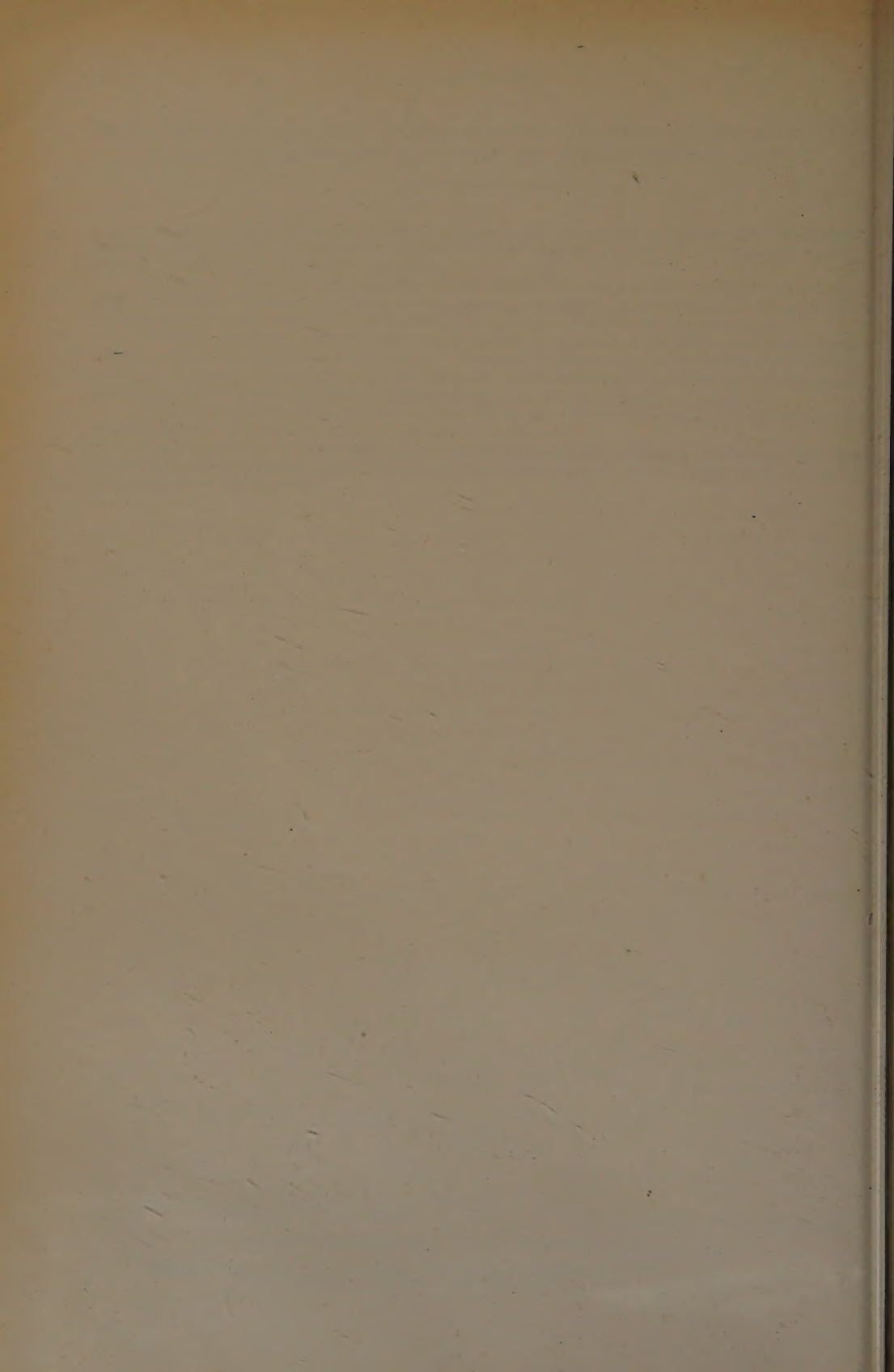
Приведенными в текстовой части многочисленными кривыми, полученными при проведении дифференциально-термических анализов, автор желает облегчать геологам идентификацию минералов.

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